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The Effect of Extinguishing Agents on Burning Sonobuoys Containing Lithium-Sulfur Dioxide Batteries

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FOREWORD

The work described in this report was initiated in January 1984 under the title, "Aircraft Subsystem Fire Response: Lithium Battery Fire Response Characterization," under program element 63262N-W0592 funded by the Naval Air Systems Command. Since lithium metal reacts vigorously with water and most other common fire extinguishing agents, there was concern as to what might happen in a deck fire involving large numbers of lithium containing batteries.

The experimental work for the first phase of the investigation was concluded in February 1986. An additional sonobuoy burn involving firemen is currently under consideration but does not involve the use of any new fire extinquishing materials. Another phase of this ongoing task is to determine the hazards, if any, associated with the cleanup and disposal of lithium-sulfur dioxide batteries that have been exposed to a fire which may have had an extinguishing agent applied. The concern in this case is whether such batteries will be sensitive to the shock and crushing that could be expected in a cleanup following a fire.

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(U) Aqueous film forming foam (AFFF), carbon dioxide, Halon 1211, and water have been applied to burning sonobuoys containing lithium-sulfur dioxide. No chemical reactions were observed between the fire-extinguishing materials and the lithium of the batteries. Water-reactive lithium (and aluminum) compounds that could release large quantities of explosive acetylene, hydrogen, and methane were found in the incinerated batteries. The nature and amount of gas formed by the reactions with water indicates that most of the lithium remains inside a battery during a fire. The batteries were observed to vent sulfur dioxide as late as an hour after the initiation of the fire.

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INTRODUCTION

    When lightweight, portable, electrical power supplies are needed
for a military application, the use of a battery having an anode made of
lithium metal may be required. Lithium has a low-equivalent weight and
is the most electronegative element that is solid at normal tempera-
tures. When used with sulfur dioxide as the catholyte, acetonitrile as
the solvent, and lithium bromide as the electrolyte, a high-energy
density battery is formed. Carbon black pressed onto an aluminum screen
is often used as the current collector for these lithium-sulfur dioxide
battery cells.

    Sonobuoys use the majority of lithium batteries within the Navy.
Lithium batteries can be found in: the AN/SSQ-53B; the AN/SSQ-62, 62A,
and 62B; and in the AN/SSQ-77A sonobuoys (Reference 1). Since the sono-
buoys are produced by different manufacturers, all of the sonobuoys may
not necessarily have lithium batteries. Of these sonobuoys, the
AN/SSQ-62s contain the greatest amount of lithium, up to 48 grams
(Reference 2).

    Although lithium-sulfur dioxide batteries have been in use for many
years, the Navy considers them **hazardous at all times**. "Incidents have
been documented involving the venting of toxic gases, fires and explo-
sions" (Reference 3). Separate from the problems of the batteries,
lithium metal, particularly when above its melting point of 180°C, is
spontaneously flammable in air and detonates violently after reacting
with components of combustion and fire extinguishing agents such as
water and the halogenated hydrocarbons (Halons) (Reference 4). All of
these factors indicated that inflamed sonobuoys that contain lithium
batteries might very well present some unexpected hazards to anyone
attempting to extinguish them. The purpose of this report is to
disclose the results of laboratory and field tests that were performed
at the Naval Weapons Center to determine whether lithium-sulfur dioxide
batteries introduced any special hazard to the problems of extinguishing
burning sonobuoys that have been ignited by burning JP-5 fuel. Condi-
tions were selected to simulate what might occur if an aircraft carrying
sonobuoys were to crash on the deck of a ship.

THE FIRE AND THE SONOBUOYS

ATTITUDE OF THE SONOBUOYS

The attitude of a sonobuoy plays an important role in its response to a fire. This is particularly true when the sonobuoys are close packed, e.g., in their shipping container. The temperature of a JP-5 fire easily reaches 2000°F (1093°C). This is well above the melting point of aluminum metal (660°C), a major component of the outer skin of sonobuoys. If the sonobuoy is standing in a vertical position, most of the melting aluminum drips onto the deck. On the other hand, when the sonobuoy is in a horizontal position, the molten aluminum falls onto other sonobuoy components causing reactions. Many of the large holes that were found in the cases of the lithium-sulfur dioxide cells after incineration appear to be caused by molten aluminum.

When sonobuoys are shipped in large quantities, they are placed in a vertical position on a pallet (Reference 1). The spaces between contiguous sonobuoys create chimneys for the flow of hot gases and flames. This flow pattern is not as pronounced for sonobuoys that are in a horizontal position. In fact, sonobuoys on the bottom of a horizontal stack may be protected from the heat generated by vertical flames.

Smaller quantities of sonobuoys are transported in a horizontal position (Reference 1). Thus, we decided that we should have sonobuoys in both horizontal and vertical positions in the burn tests. Since four sonobuoys represented the smallest symmetrical grouping that would simulate large stacks, each of our tests used four sonobuoys stacked in a vertical position and four sonobuoys stacked in a horizontal position.

THE SONOBUOYS

Since the AN/SSQ-62 sonobuoys contain the largest amount of lithium (Reference 1), we used these sonobuoys predominantly. We attempted to have all eight sonobuoys used in a burn be of the same type, from the same manufacturer, and having the same Navy Ammunition Logistics Code (NALC) number. Since the NALC number primarily differentiated the type of fall-retardation devices, either in air or through the water, we soon relaxed our requirement to have all of the sonobuoys in a given burn have the same NALC number. Although it might be informative to determine the effects of different extinguishing materials on different sonobuoys, such a determination would be extremely expensive. For the AN/SSQ-62 sonobuoys, alone, there are three major types, 62, 62A, and 62B. Each of the three manufacturers of sonobuoys construct them under different contract numbers, in different years, and with a number of different NALC numbers. Compound the above parameters with different extinguishing agents that could be applied at different times over a

range of 60 minutes onto sonobuoys standing in different configurations with and without their protective gray plastic overpacks and it becomes obvious that some degree of selection of the experiments was necessary.

THE FIREBOX

Figure 1 shows the firebox (8 feet wide by 8 feet long by 10 feet tall) loaded with eight sonobuoys in their plastic overpacks. The sono-buoys were mounted 5 feet above the bottom of the firebox on solid steel
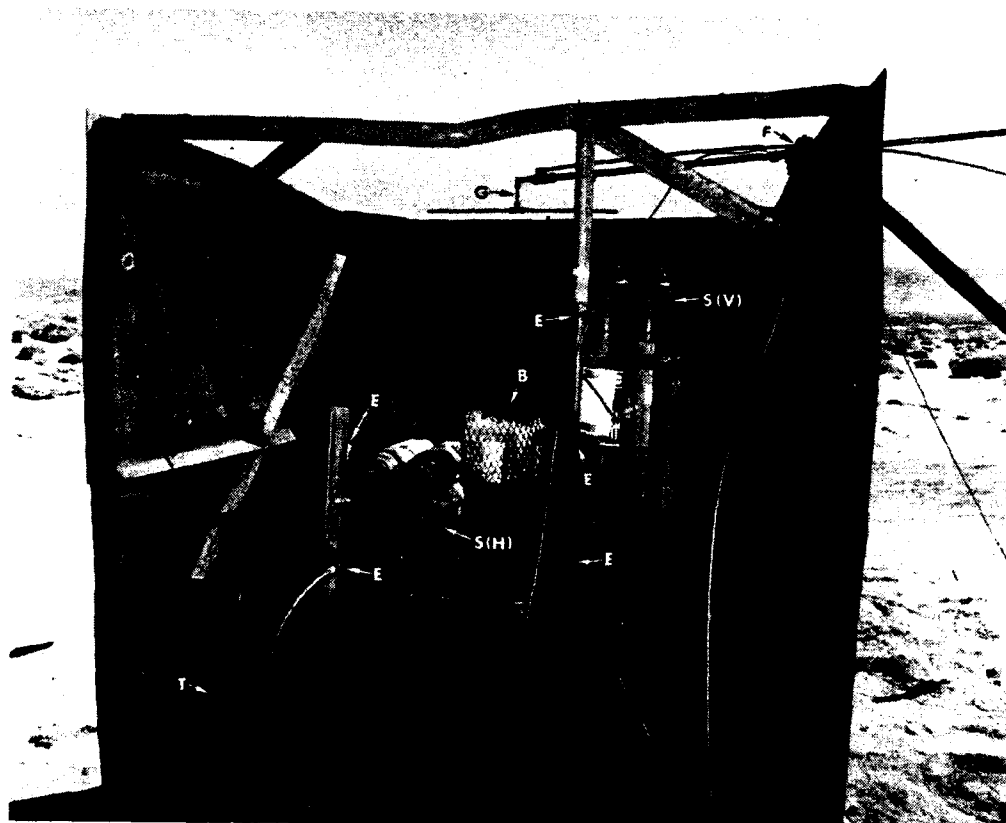
FIGURE 1. Firebox Loaded with 8 Sonobuoys. (B) Basket of bat-teries, (E) ports for application of extinguishing materials, (G) port for sampling of gases, (F) port from which JP-5 is sprayed into the firebox, (S(H)) sonobuoys stacked in a horizontal position, (S(U)) sonobuoys in a vertical configuration, (T) one of the thermocouples.

platforms having a 1-inch lip around the edge to contain any molten metal at the base of the sonobuoys. A metal, mesh screen was located a foot below the steel platforms to prevent large sonobuoy components (such as batteries) from falling to the bottom of the firebox and, consequently, not receiving the full heat of the fire. Because of

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safety considerations, it was considered advisable to incinerate all battery cells so they would release their sulfur dioxide in the fire and, thus, there would be a reduced hazard when the battery cells were collected after the incineration process was concluded. Figure 2 shows the general lay-out of the sonobuoys and their associated thermocouples with respect to the firebox.
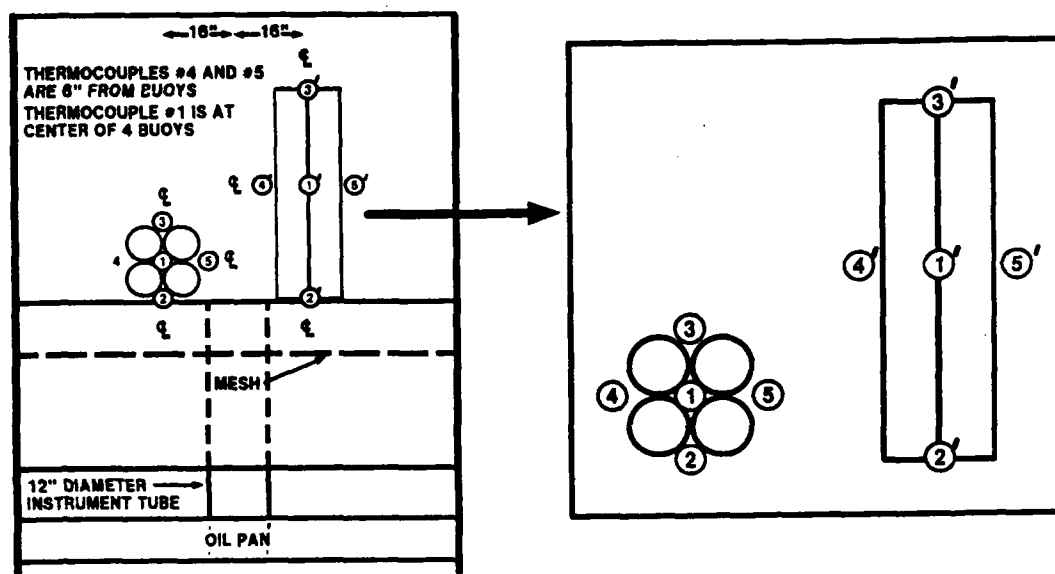

FIGURE 2. Firebox Showing Location of the Thermocouples.

TEMPERATURE MEASUREMENTS

Although the objective of the present tests was not considered to be a cook off, the locations of most of the thermocouples used to measure temperature were patterned after those used for cook off tests (MIL-STD-1648A(AS)). Since our tests took much longer than a cook off does, the frequency of temperature measurements were 1/10 seconds rather than 1/second. In addition to the 10 thermocouples shown in Figure 2, an 11th was used to measure the temperature of the firebox (it was located inside the space formed by a piece of angle iron welded to the side of the firebox). Placement of one of the thermocouples is shown in Figure 1.

CONTROL OF THE FIRE

The firebox was designed to hold liquid fuel, such as JP-5, in the bottom of the box. When operated in this mode, once started, the fire would burn until the fuel was exhausted (or the fire knocked down using a fire-extinguishing agent). A JP-5 fire creates a considerable amount of smoke and, consequently, obscures the condition of the sonobuoys.

But even more important, the use of a fire-extinguishing agent, such as water, would have floated the JP-5 out of the pan onto the ground and, hence, would have contaminated the area. If a foam were used, such as aqueous film forming foam (AFFF), the fire would be difficult to restart in order to completely incinerate the sonobuoys and their associated batteries.

In order to overcome the above problems, a dual, controlled, fuel source was used. A rack using 100 propane nozzles was placed at the bottom of the air gap shown in Figure 2. Two electrically controlled sparks (from igniters used to start jet aircraft) were used to ignite the propane remotely. From the top of the firebox, a stream of JP-5 was directed at the horizontal sonobuoys, and a second stream of JP-5 was directed at the vertical sonobuoys. The location of the nozzle for this application of JP-5 is indicated in Figure 1. The section of pipe that was close to the firebox was cooled by water. The JP-5 could also be remotely controlled through activation of a pump and/or an electrically controlled valve. This source of JP-5 could also be used to soak the sonobuoys either prior to the initiation of the propane fire or after the sonobuoys had been subjected to a fire-extinguishing agent. When the sonobuoys had been pre-soaked with JP-5 during the test, the temperature of the firebox would rise very quickly under conditions similar to those anticipated for a crashed aircraft. When the JP-5 was applied after the application of a fire-extinguishing agent, it was possible to determine how effective the agent was in extinguishing flames and in cooling hot spots internal to the sonobuoys.

The control of these two fuels greatly improved the tests. When the propane was activated, the sound of the flowing gas masked the events occurring with the sonobuoy components. Although the JP-5 was a much quieter fuel, the intense color of its flames visually masked the sonobuoys. Since it was possible to turn off both fuel sources, it was now possible to closely listen to and observe the sonobuoys and to also test the effects of the fire-extinguishing agents on just burning sonobuoys.

GASES FROM BURNING SONOBUOYS AND VENTING BATTERIES

Fauth and Lay made a study of the incineration of lithium-sulfur dioxide batteries (Reference 5). They reported that sulfur dioxide appeared to be unaffected by the combustion of fuel oil. We constructed a simple laboratory-scale burner (shown in Figure 3) where JP-5 was used as a fuel. We wanted to know if the large amounts of carbon soot released from a JP-5 fire might adsorb the sulfur dioxide. We could determine a slight decrease in the amount of sulfur dioxide (measured by ultraviolet (UV) spectroscopy) caused by passing it into the JP-5 laboratory-scale burner primarily when the flow of air was markedly decreased. Consequently, from our results, and those of Fauth and Lay, most of the sulfur dioxide would be released into the atmosphere from lithium-sulfur dioxide batteries involved in a fire.
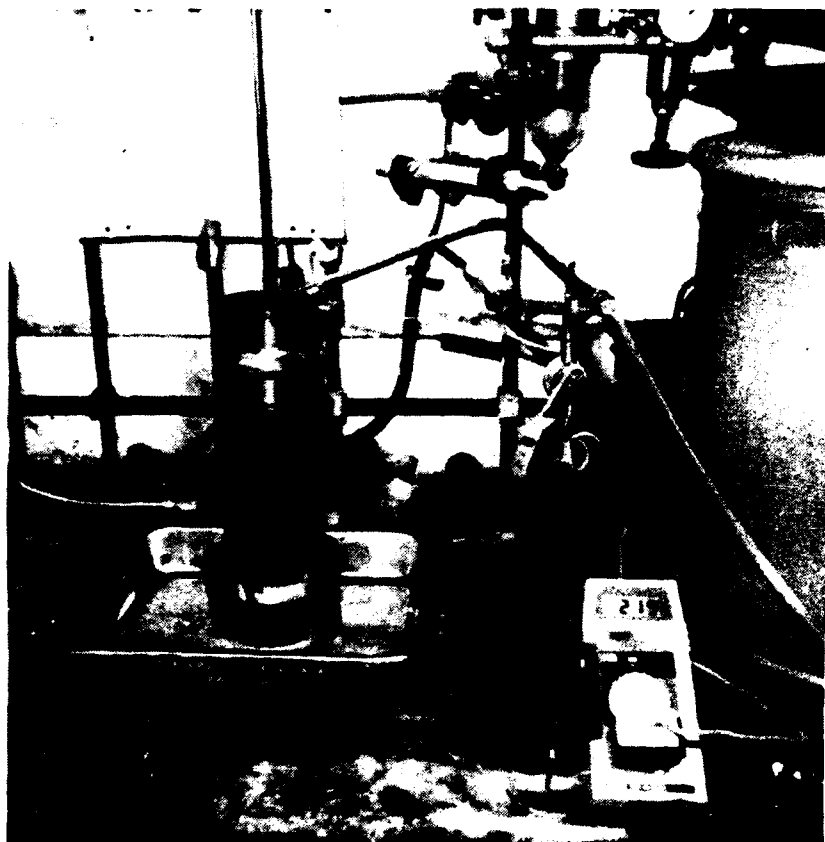
FIGURE 3. Laboratory-Scale Burner for Measuring
Effects of Burning and Soot on Sulfur Dioxide.

A gas-sampling system was constricted to detect when sulfur dioxide
was released during the course of a burn. This release of sulfur
dioxide would, in turn, indicate the time of venting of the batteries.
Figure 4 shows the gas-sampling board that was capable of holding eight
"grab samples." The gas-sampling board should have been able to
continuously monitor the sulfur dioxide concentration. Unfortunately,
the sulfur dioxide probe from Lazar Research Laboratories, Los Angeles,
Calif., that was to provide a continuous record of sulfur dioxide
measurements had a few problems. Although advertised as being capable
of making measurements on "stack gases," in reality, the measurements
had best be performed on solutions which had stack gases bubbled through
them. We found that reasonable measurements could be performed on the
gases above a solution of sulfur dioxide in water, however, the results
were not reproducible. Furthermore, it was possible to make measure-
ments going from low to high concentrations in either the gas or liquid
phase, but not the reverse. The Lazar probe operates by the diffusion
of sulfur dioxide through a membrane and, in essence, measures the acid

concentration on a small volume of solution inside it using a glass and a reference electrode. Once a high concentration of sulfur dioxide has passed through the membrane, however, the probe requires a considerable period of time for the sulfur dioxide to diffuse so that low concentrations can be measured again. In addition, where one probe would produce a positive voltage with increasing sulfur dioxide concentrations, a second probe supplied a negative voltage, while a third probe gave no response. We finally gave up on trying to make continuous sulfur dioxide measurements and had to rely on our eight grab samples.
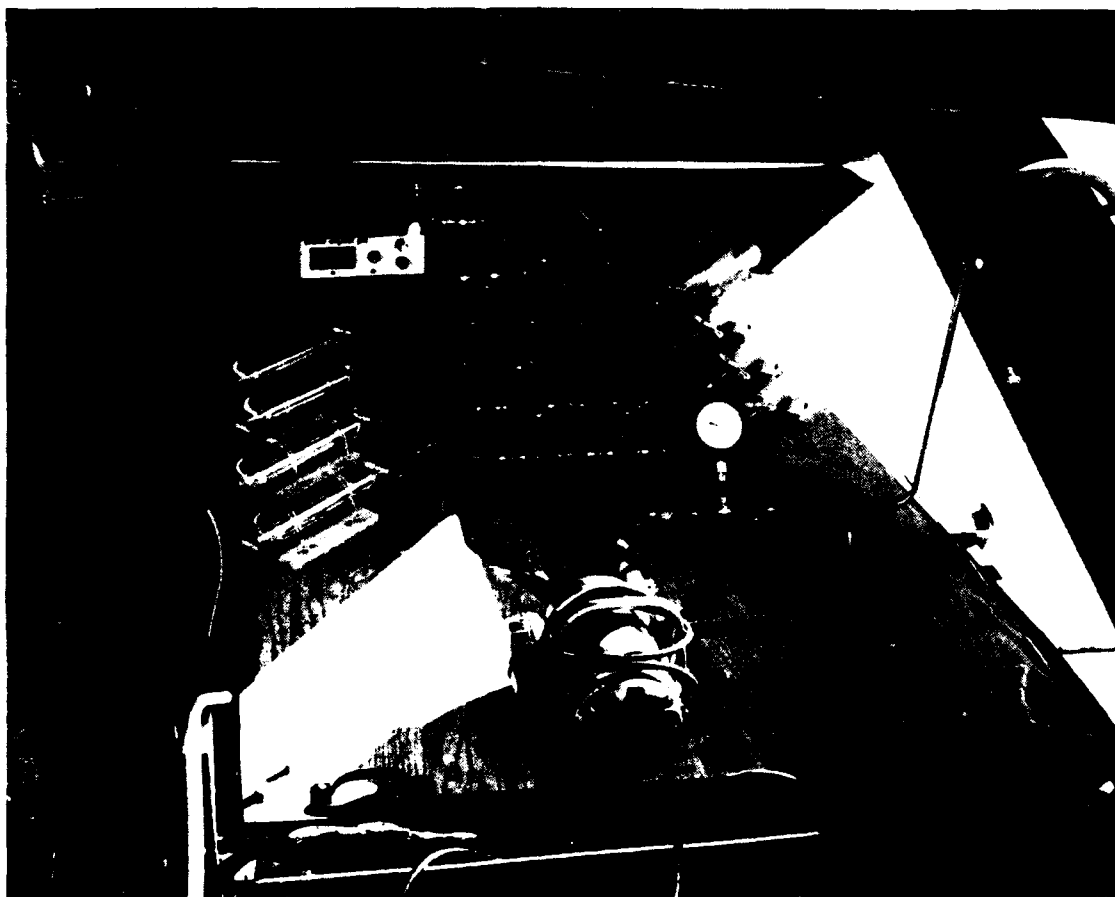
FIGURE 4. Gas Sampling Board.

With only eight sample containers, there is a very real problem when the sampling should be done. Our solution was to sample four of the bottles at predetermined periods during the burn and to sample the other four when some observable "event" occurred. This event was usually a loud noise with a corresponding movement of sonobuoy components or a puff of smoke. There was approximately 5 seconds between the observation of an event and the start of the sampling. Our sampling of the gases in the firebox was from the top of the box using water-cooled, 1/2-inch stainless steel tubing (Figure 1). The gas-sampling board was located behind a heavy steel shield 40 ft from the firebox. Once the

decision to open the electrically controlled valve was made, it took about 20 seconds for the bottle to reach the same pressure as the gas flowing past its opening.

For our first few burns, we would continually pull gas through our sampling system. Because of our concern that some of the sulfur dioxide could be adsorbed onto carbon soot, we switched the sampling system to pump air from the gas sampling system to the top of the firebox until we were ready to sample the gas. This procedure greatly minimized the amount of carbon soot that would have otherwise collected in the tubing leading to the sampling board. This procedure precluded using the LAZAR sulfur dioxide probe in a continuous manner but this was no great loss since this probe had such a poor response to sulfur dioxide in the gas phase.

In burns 7, 8, and 9, we placed some of the evacuated sample flasks and their associated electrically controlled valves at various locations about 6 feet from the sides or back of the firebox. One of these bottles was opened at the same time that a sample was taken at the top of the firebox. In no case did we measure sulfur dioxide in the sample flasks located just outside the firebox. In burns 6 through 9, we included, in addition to the sonobuoys, a basket of 13 batteries (each battery consisted of 14 Duracell LO-30SH cells for a total of 182 extra cells) (see Figure 1). The extra batteries could be viewed during the course of the burn and apparently supplied the additional sulfur dioxide needed to show up in the gas sampling bottles. Only after we had added the basket of batteries did we observe heavy concentrations of sulfur dioxide.

FIRE EXTINGUISHING MATERIALS

In addition to water, AFFF, Halon, dry chemicals, and carbon dioxide are the usual materials used for the extinguishment of aircraft fires (Reference 6). Except for dry chemicals, we tested all of these materials on burning sonobuoys (since dry chemicals are being phased-out aboard ships, we did not want to include them in our tests). The AFFF was applied from a remotely controlled system at a rate of about 100 gal/min. The other fire-extinguishing materials were applied from the nozzle system shown in Figure 1. This smaller extinguishing system could also be remotely controlled. Although there are other types of extinguishing materials that have been proposed for the specific extinguishment of burning metals (Reference 7 and 8), it was not considered necessary to apply them when it became obvious that any combustion effects due to the batteries were insignificant compared to those of the sonobuoy components and the JP-5. In addition, the types of extinguishment materials, such as carbon spheres, that have some degree of success on metal fires, would very likely, not only not extinguish a JP-5 fire,

but rather would add to the conflagration. Since all of the extinguishment materials that were used are noted for being very reactive with molten lithium (References 4 and 8), the failure to observe any untoward reactions that could be ascribed to the batteries when these materials were applied was considered additional reason to not need any of the metal fire-extinguishing materials, i.e., the standard extinguishment materials were effective (to differing degrees) in controlling the fires.

We were particularly interested in the effectiveness of AFFF and the Halons. Aqueous film forming foam extinguishing systems are used, for example, on the flight deck, hanger deck, well deck, and vehicle stowage area on ships (Reference 9); Halon systems are installed on many Navy ships in selected locations (Reference 10).

THE BURNS

BURN 1

The first burn was on 8 June 1984 and used eight AN/SSQ-62 sonobuoys in their plastic overpacks manufactured by Sparton Electronics Division, Jackson, Miss. The JP-5 fuel was in the bottom of the firebox. No gas sampling was performed in this preliminary test. Figure 5 shows the average temperature of thermocouples 1, 3, and 5 for the sonobuoys located in the horizontal stack, as well as the average temperature for thermocouples 1', 3', and 5' of the vertical stack of sonobuoys. The highest temperature observed in this test (or any of the tests) was 2500°F (1371°C) for thermocouple 2' located at the base of the vertical stack of sonobuoys. We assumed that an aluminum fire was being observed. The first events were observed (primarily heard) at 11 minutes after the initiation of the fire; the events terminated at about 18 minutes after initiation of the burn.

One of the interesting features of burn 1 was the detection of eight different radio waves that were in the vicinity of those anticipated for sonobuoys. These radio emissions were detected from 18 to 44 minutes after the ignition of the fire and were not detected during the same time period on the next day. We had these measurements performed since we considered that the heat of the fire might activate the radios of the sonobuoys. These measurements were made some distance from the test site and proved to be extraneous with respect to the sonobuoys. During burn 2, a mobile van was located close to the test site, and no radio waves associated with the sonobuoys were detected.

An examination of the physical condition of the incinerated batteries after the conclusion of burn 1 showed 74% of the batteries could be considered intact and 26% had large holes and open vents.

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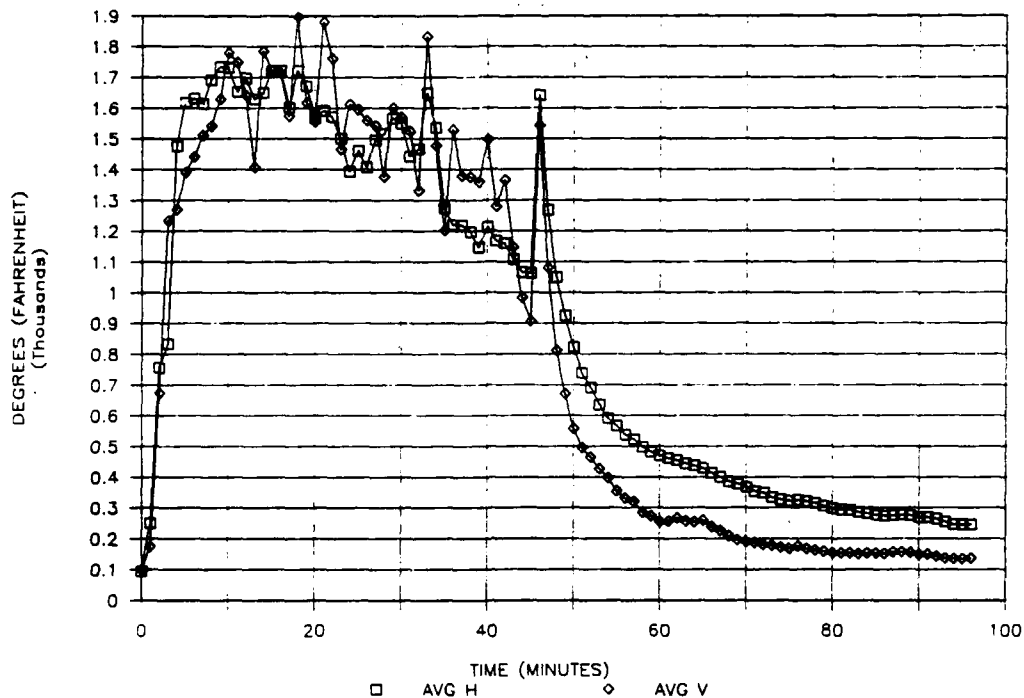
FIGURE 5. Average Temperatures of Burn 1 for Horizontal (H) and Vertical (V) Sonobuoys. Only thermocouples 1, 3, and 5 are used to determine average values.

BURN 2

Burn 2 was on 4 October 1984 in the same fashion as burn 1 using JP-5 in the bottom of the firebox. AN/SSQ-62A sonobuoys were used for this test. Figure 6 shows the average temperatures observed for both the horizontal as well as the vertical sonobuoys. Much less JP-5 was used for burn 2 than for burn 1; compare the shorter period of high temperatures of Figure 6 with those in Figure 5. The peaks and valleys of the temperatures measured in the vicinity of the horizontal sonobuoys match fairly closely to those of the vertical sonobuoys in Figures 5 and 6. These fluctuations are due no doubt to variations in the direction and velocity of the wind with respect to the firebox as well as being to the temperatures of the various components inside the firebox (and the firebox itself).
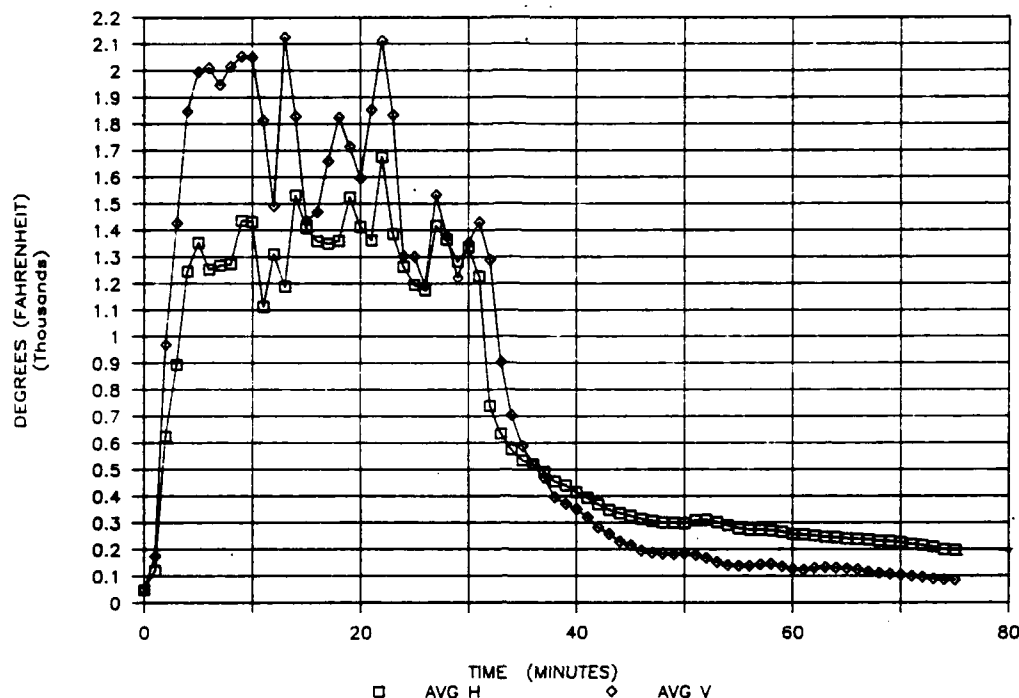
FIGURE 6. Average Temperature of Burn 2 for
Horizontal (H) and Vertical (V) Sonobuoys.

Gas analysis was performed during burn 2, but no sulfur dioxide or
acetonitrile were detected within the limits of infrared (IR) spectro-
photometric analysis. For this reason, laboratory tests were initiated
to determine whether major amounts of sulfur dioxide could be removed by
the soot from a JP-5 fire. A more sensitive technique using UV spec-
troscopy in 10-cm long cells was used for the laboratory tests. As
indicated earlier, no major decrease in the sulfur dioxide concentration
was observed in the laboratory tests under normal conditions of
burning. The time that samples were taken after the start of a burn are
shown in Figure 7. Since IR spectroscopy did not have sufficient sensi-
tivity in the 10-cm cells that we used, gas chromatography (GC) was used
to determine the amount of sulfur dioxide in burn 2.

Events were observed from 6 to 58 minutes after the ignition of the
fire. A total of about 74 events were counted.

In burn 2, an evaluation of the external condition of the inciner-
ated batteries was also performed. Ninty-one of a possible 96 batteries
were recovered. Thirty-one of these batteries had an appearance of
having no openings, i.e., their vent holes appeared to be sealed; 28 of
the batteries had open vent holes and 32 batteries were either destroyed
or had at least one large hole.

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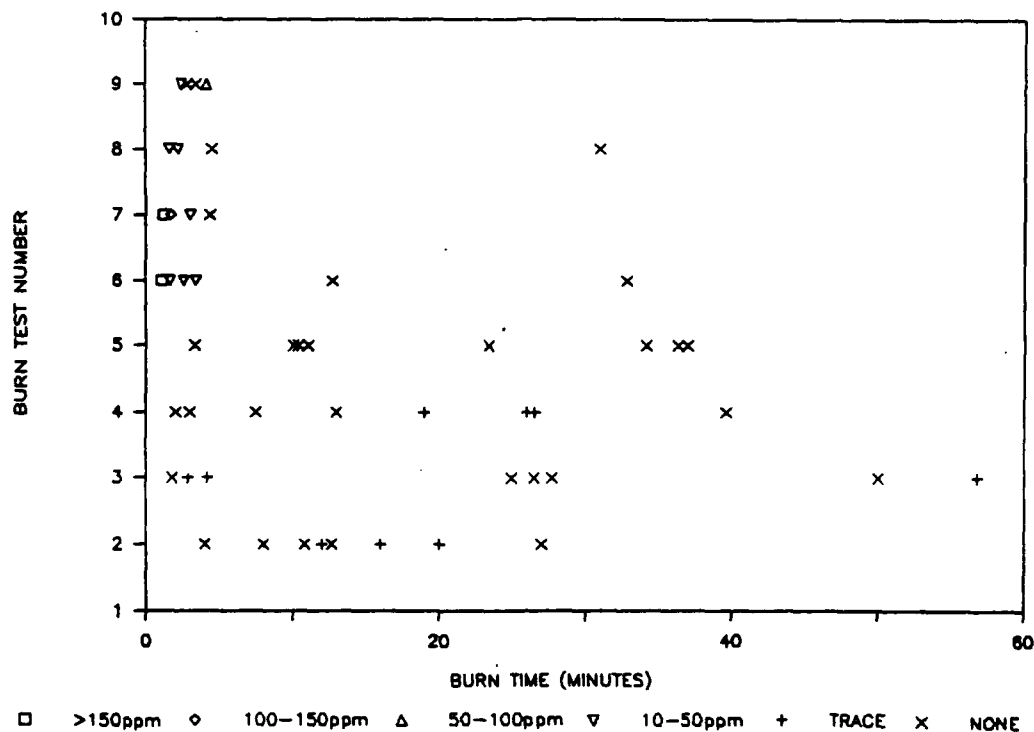
FIGURE 7. Tests for Sulfur Dioxide in Burns 2 Through 9.
Sulfur dioxide was determined by GC.

BURN 3

Burn 3 was on 8 January 1985 and used propane burners underneath and a JP-5 fuel source above the sonobuoys. Eight sonobuoys were again tested. A typical test plan is given in Appendix A. AFFF was used as an extinguishing agent. Figure 8 shows the time sequence and a condensation of most of the results of this test for the horizontal buoys. The temperatures of burn 3 were not as high as those of the previous two burns because of the attempt to use propane as the primary fuel. In later burns, more JP-5 was applied with resulting higher temperatures. As can be seen in Figure 8, the extinguishing material, AFFF, was applied at about 8 and 18 minutes after ignition of the fire. It was effective in both cases with no obvious lithium-water fires being observed. By the end of the second application, enough water was in the bottom of the firebox to make it difficult to obtain high temperatures in the firebox with propane. For subsequent tests, a large drain was added to minimize this effect. It should be noted that events occurred as late as 80 minutes after first ignition of the fire. Not indicated in Figure 8 is the effect of application of JP-5 on the extinguished sonobuoys. Within a few seconds of this application of JP-5, the sonobuoys re-ignited. We assumed that this was due to "hot-spots" and/or flames internal to the sonobuoys.

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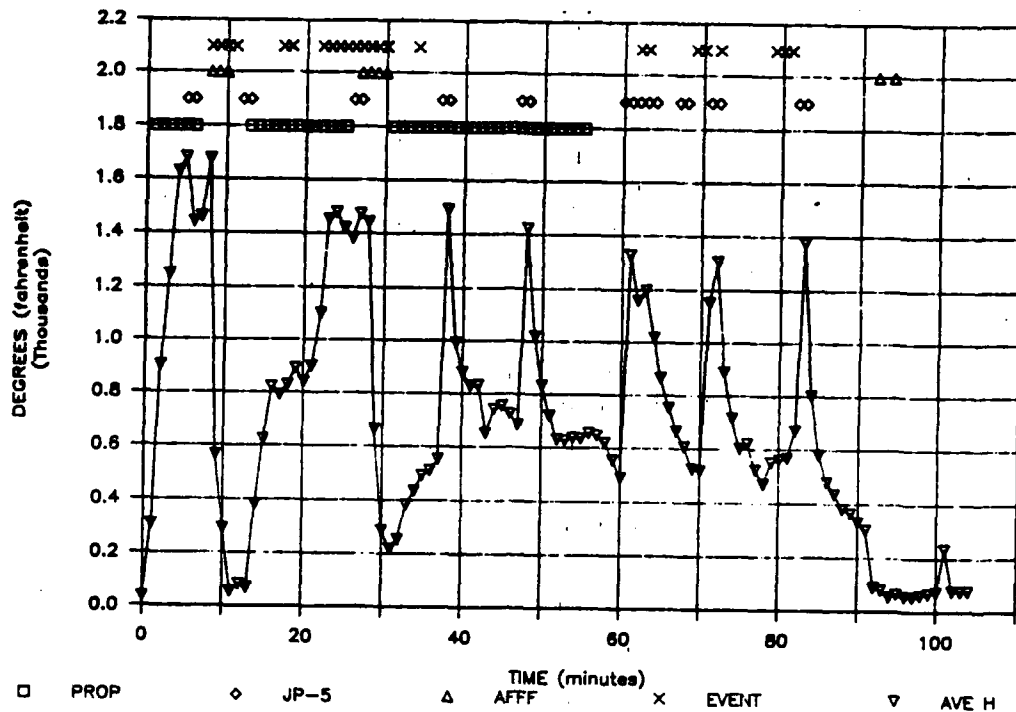
FIGURE 8. Average Temperature for Horizontal Sonobuoys in Burn 3.

The examination of the incinerated batteries left from burn 3 showed 53% could be considered intact and 47% had large holes and open vents.

BURN 4

Burn 4 was on 16 January 1985. Figure 9 shows the average temperature of the horizontal sonobuoys. This test also used AFFF for an extinguishing material. This test was performed on seven sonobuoys that had been manufactured by Raytheon Co., Portsmouth, R. I., and one manufactured by Sparton. As was standard, all of the sonobuoys were in their overpacks. More JP-5 was applied than in Burn 3 and the first application of AFFF was much later into the burn (16 minutes). Sixteen minutes is the middle of the occurrence of the major events. The AFFF was again effective in extinguishing the fire, and no significant explosions or fires were observed that would indicate any significant chemical reactions between lithium metal and AFFF. Events were again observed well after 80 minutes from the initiation of the fire and well after the last application of fuel.

The examination of the incinerated batteries remaining after this burn showed that 86% appeared intact.
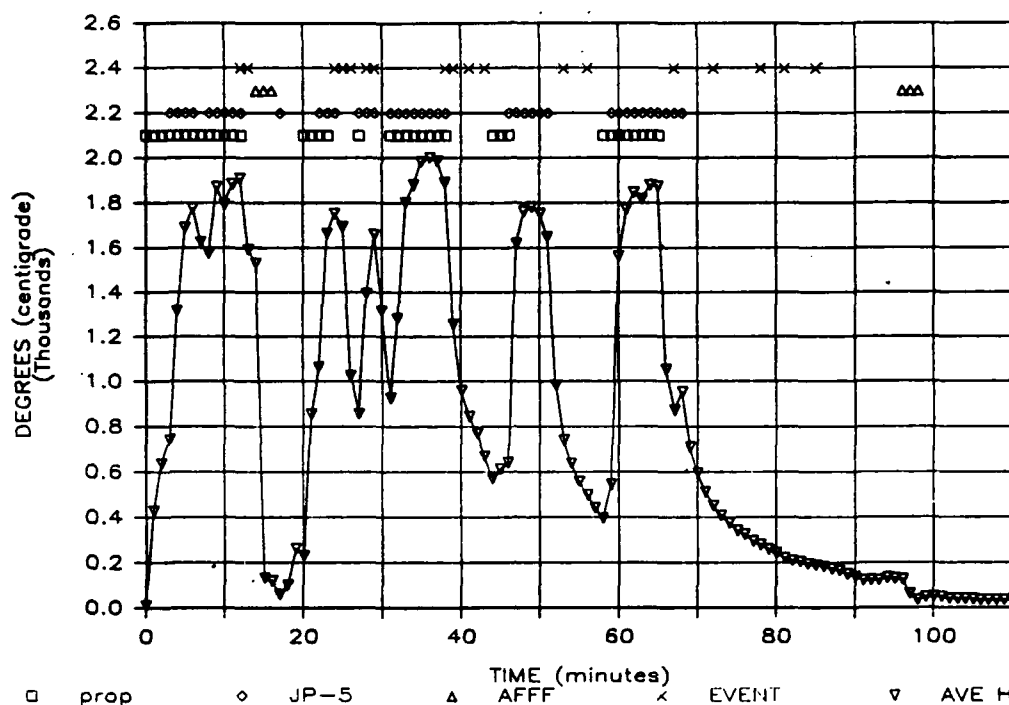
FIGURE 9. Average Temperature for Horizontal Sonobuoys in Burn 4.

BURN 5

Burn 5 was on 3 May 1985. Extinguishment was not of interest in this burn so the AFFF was only applied at the conclusion of the burn in order to cool down the firebox more rapidly. This cooling step became part of our standard procedure starting in burn 3. Burn 5 was performed on AN/SSQ-62 sonobuoys that had their lithium-sulfur dioxide batteries removed. Thus, the events shown in Figure 9 occurred as a result of the explosion of the squibs and carbon dioxide cylinders used to inflate the sonobuoys. Burn 5 demonstrated that the loud events were not due to the batteries.

BURN 6

In order to gain a better perspective of what the batteries were doing in these sonobuoy fires, 13 Duracell batteries, each containing 14 LO-30SH cells, were placed in a basket between the horizontal and the vertical sonobuoys. Thus, there were 182 lithium-sulfur dioxide cells in addition to those located within the sonobuoys. The first test including this basket was on 7 May 1985. Halon 1211 was the extinguishing material used for this test. Four 19-1b Halon 1211 fire extinguishers were used as a source of the Halon. This Halon could be applied to either the vertical sonobuoys, to the horizontal sonobuoys,

or both through the electrically controlled system shown in Figure 1. Nothing was observed that would suggest any significant reaction of Halon 1211 with lithium metal present inside (or outside) the batteries. Hot lithium is known to react violently with Halons (Reference 4).

Although the average temperatures of burn 6 (shown in Figure 10) were above 1000°F for at least 20 minutes and were as high as 1600°F for
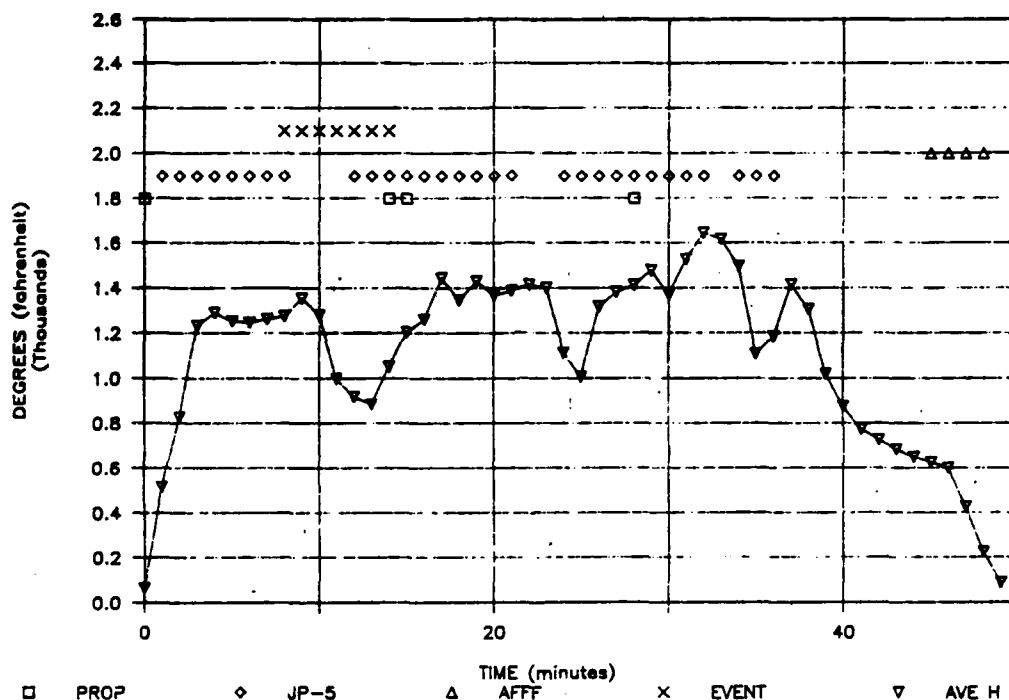
FIGURE 10. Average Temperatures for Horizontal Sonobuoys in Burn 5.

short periods, two battery packs from the horizontal sonobuoys were not only intact, but showed voltages on most of the cells. The labels on the batteries were still readable. This observation explains why only small amounts of sulfur dioxide were found when the basket of batteries wasn't in the burn and why events and traces of sulfur dioxide were detected so late into the burns. It is apparent that the sonobuoys insulate the batteries from the effects of the fire quite well. This is particularly true when the sonobuoys are semi-protected from the flames by the surface upon which they rest. The vertically stacked sonobuoys do not have this protection. In addition, the spaces between the vertical sonobuoys serves as a chimney for the hot gases and flames. Thus in a fire, the vertical sonobuoys are more quickly consumed than are the horizontally stacked sonobuoys. Since the venting of the batteries located inside the sonobuoys was spread over 80 minutes and likely did not start until after 8 minutes, it would be rather difficult to sample at the exact time of venting. Furthermore, the strong drafts of air

associated with the fire would greatly dilute the sulfur dioxide. Only when we had a large number of lithium-sulfur dioxide cells in an uninsulated condition, i.e., the basket of batteries, did we detect concentrations of sulfur dioxide greater than 100 ppm.

TABLE 1. Cell Gas Generation Test Results.

Test No.	Date tested	Burn No.	Basket/ vertical/ horizontal	Vented/ unvented	Holes[a]	Wt, g	V_{STP}, ℓ[b]
1	6/7/85	6	Horizontal	Unvented	...	47.0	5.45
2	6/7/85	6	Horizontal	Vented	T & B	48.0	3.28
3	6/10/85	6	Horizontal	Unvented	...	47.0	5.43
4	6/10/85	6	Horizontal	Unvented	...	48.0	4.61
5	6/10/85	6	Horizontal	Unvented	...	47.0	6.28
6	6/10/85	6	Horizontal	Vented	T	47.0	7.24
7	6/11/85	6	Vertical	Unvented	...	47.0	5.83
8	6/12/85	6	Vertical	Vented	B	46.0	4.52
9	6/12/85	6	Vertical	Vented	T	48.5	0.00[c]
10	6/12/85	6	Vertical	Vented	T	48.0	3.39
11	6/12/85	6	Vertical	Unvented	...	47.5	6.32
12	6/13/85	6	Vertical	Vented	T	48.5	5.21
13	6/14/85	6	Vertical	Vented	T & B	47.5	5.60
14	6/14/85	6	Basket	Vented	T	36.5	2.81[d]
15	6/14/85	6	Basket	Vented	T & S	38.5	0.59[d]
16	6/14/85	6	Basket	Vented	T	36.0	2.33[d]
17	8/6/85	6	Horizontal	Unvented	...	47.0	5.97
18	10/11/85	6	Basket	Vented	T	36.5	2.21[d]
19	10/11/85	6	Basket	Vented	T	37.0	1.66[d]
20	10/11/85	6	Basket	Vented	T	38.5	2.84[d]
21	10/11/85	6	Basket	Vented	T	37.5	1.78[d]
22	10/15/85	6	Basket	Vented	T	38.5	1.73[d]
23	19/15/85	6	Basket	Vented	T	36.0	3.63[d]
24	10/15/85	6	Vertical	Vented	T	47.0	5.43
25	10/15/85	6	Vertical	Vented	T & B	47.5	4.78
26	10/16/85	6	Vertical	Vented	T	47.5	0.00[c]
27	10/16/85	6	Vertical	Vented	B	48.0	3.03

See footnotes at end of table.

TABLE 1. (Contd.)

Test No.	Date tested	Burn No.	Basket/ vertical/ horizontal	Vented/ unvented	Holes[a]	Wt, g	V_{STP}, ℓ[b]
28	12/10/85	7	Horizontal	Vented	T	54.0	−0.27
29	12/10/85	7	Horizontal	Unvented	...	47.0	5.39
30	12/10/85	7	Horizontal	Unvented	...	47.5	5.77
31	12/10/85	7	Basket	Vented	T	38.0	0.67[d]
32	12/10/85	7	Basket	Vented	T	37.5	1.58[d]
33	12/11/85	7	Basket	Vented	T	36.5	0.63[d]
34	12/11/85	7	Basket	Vented	T	38.0	1.23[d]
35	12/11/85	7	Basket	Vented	T	37.5	1.44[d]
36	12/11/85	7	Basket	Vented	T	39.0	0.37[d]
37	12/11/85	7	Vertical	Vented	T	47.0	6.32
38	12/12/85	7	Vertical	Vented	T	48.5	3.93
39	12/12/85	7	Vertical	Unvented	...	48.5	5.64
40	12/12/85	8	Horizontal	Vented	T	63.0	0.01
41	12/12/85	8	Horizontal	Unvented	...	60.0	−0.09
42	12/13/85	8	Horizontal	Vented	T	51.0	5.27
43	12/13/85	8	Basket	Vented	T	39.0	1.27[d]
44	12/13/85	8	Basket	Vented	T	36.0	3.01[d]
45	12/16/85	8	Basket	Vented	T	37.5	0.95[d]
46	12/16/85	8	Basket	Vented	T	39.0	3.11[d]
47	12/16/85	8	Basket	Vented	T	40.0	1.55[d]
48	12/16/85	8	Basket	Vented	T	37.5	0.93[d]
49	12/18/85	8	Vertical	Vented	T	56.0	0.23
50	12/19/85	8	Vertical	Vented	B	49.0	4.46
51	12/19/85	8	Vertical	Vented	T	48.5	6.08
52	12/19/85	9	Horizontal	Unvented	..	48.0	6.34
53	12/19/85	9	Horizontal	Unvented	...	47.0	5.63
54	12/19/85	9	Horizontal	Unvented	...	47.0	6.76
55	1/15/86	9	Basket	Vented	T	37.0	4.96[d]
56	1/15/86	9	Basket	Vented	T & S	41.0	0.11[d]
57	1/15/86	9	Basket	Vented	B	38.0	0.29[d]

See footnotes at end of table.

TABLE 1. (Contd.)

Test No.	Date tested	Burn No.	Basket/ vertical/ horizontal	Vented/ unvented	Holes[a]	Wt, g	V_{STP}, ℓ[b]
58	1/16/86	9	Basket	Vented	T	.37.5	3.21[d]
59	1/16/86	9	Basket	Vented	T	37.0	3.00[d]
60	1/16/86	9	Basket	Vented	T	38.0	0.00[d]
61	1/16/86	9	Vertical	Vented	T	48.5	3.91
62	1/16/86	9	Vertical	Vented	B	45.5	2.80
63	1/16/86	9	Vertical	Vented	T & B	51.0	2.14
64	1/27/86	6	Horizontal	Vented	T & B	50.0	3.59
65	1/27/86	6	Horizontal	Vented	T	49.0	5.98
66	1/27/86	6	Horizontal	Vented	T	47.0	6.28
67	1/27/86	6	Vertical	Vented	T	47.5	2.35
68	1/27/86	6	Vertical	Vented	T & B	47.5	0.98
69	1/27/86	6	Vertical	Vented	B	47.5	2.88
70	1/27/86	6	Basket	Vented	T	36.5	1.23[d]
71	1/28/86	6	Basket	Vented	T	36.5	1.71[d]
72	1/28/86	6	Basket	Vented	T	37.0	1.58[d]
73	1/28/86	6	Basket	Vented	T	36.0	1.78[d]
74	1/28/86	6	Basket	Vented	T	35.5	3.25[d]
75	1/28/86	6	Basket	Vented	T & S	43.0	0.33[d]
76	1/28/86	7	Basket	Vented	B	39.0	0.36[d]
77	1/28/86	7	Basket	Vented	S	42.5	0.18[d]
78	1/30/86	7	Basket	Vented	T	38.0	1.61[d]
79	1/30/86	7	Basket	Vented	T	37.5	2.10[d]
80	1/30/86	7	Basket	Vented	B	39.0	0.32[d]
81	1/30/86	7	Basket	Vented	T	39.0	1.62[d]
82	1/31/86	7	Vertical	Vented	B	48.0	5.93
83	1/31/86	7	Vertical	Vented	T	48.o	6.62
84	1/31/86	7	Vertical	Vented	B	51.0	2.44
85	2/3/86	7	Horizontal	Vented	T & S	48.5	1.28
86	2/3/86	7	Horizontal	Vented	T & B	50.0	2.18
87	2/3/86	7	Horizontal	Vented	T	47.5	5.90
88	2/4/86	8	Vertical	Vented	T	49.0	0.00
89	2/5/86	8	Vertical	Vented	T	51.5	2.07
90	2/5/86	8	Vertical	Vented	T	48.5	6.17

See footnotes at end of table.

TABLE 1. (Contd.)

Test No.	Date tested	Burn No.	Basket/ vertical/ horizontal	Vented/ unvented	Holes[a]	Wt, g	V_{STP}, ℓ[b]
91	2/6/86	8	Horizontal	Vented	T	50.0	2.70
92	2/6/86	8	Horizontal	Vented	T	60.0	0.31
93	2/6/86	8	Horizontal	Vented	T	59.5	0.34
94	2/6/86	8	Basket	Vented	T	36.0	2.90[d]
95	2/7/86	8	Basket	Vented	T	37.0	2.54[d]
96	2/7/86	9	Basket	Vented	T & B	38.5	0.56
97	2/7/86	9	Horizontal	Vented	B	49.0	3.33
98	2/7/86	9	Vertical	Vented	T	48.0	4.80

[a] T = top, B = bottom, S = side. [b] Volume standard temperature pressure. [c] Error in procedure, no gas measured. [d] LO-30SH rather than LO-26SH cell.
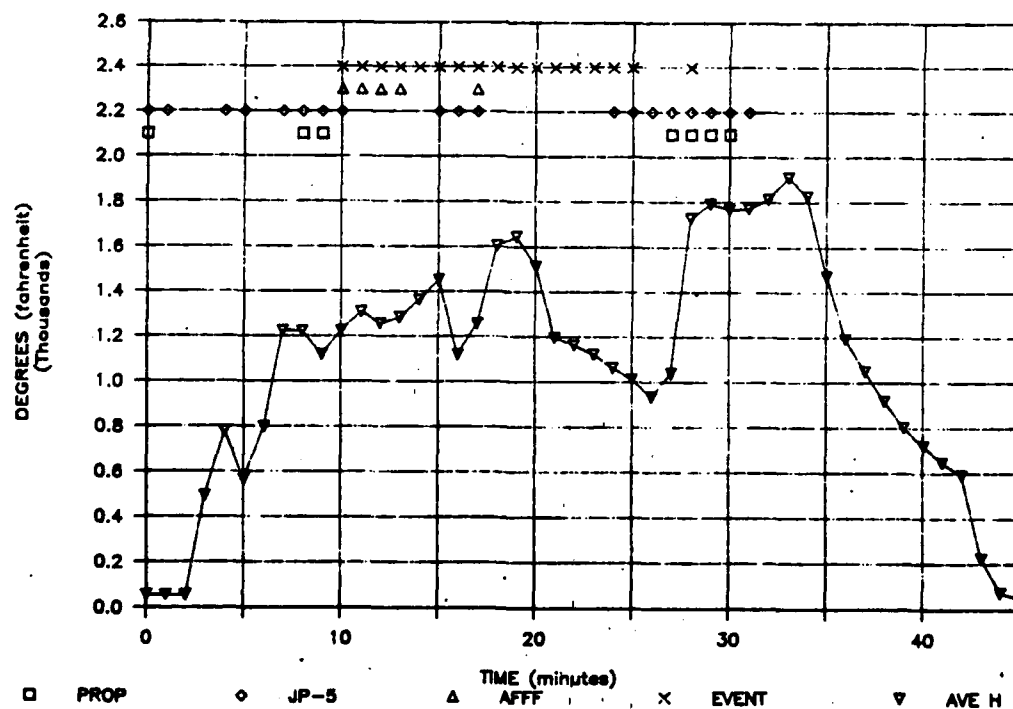

FIGURE 11. Average Temperatures for Horizontal Sonobuoys in Burn 6.

BURN 7

A second burn used Halon 1211 as the extinguishing material on sonobuoys without their protective graypacks. This was the only test performed in the series on unprotected sonobuoys. The results (shown in Figure 12) were similar to those in the previous burn. Burn 7 was on 15 May 1985.
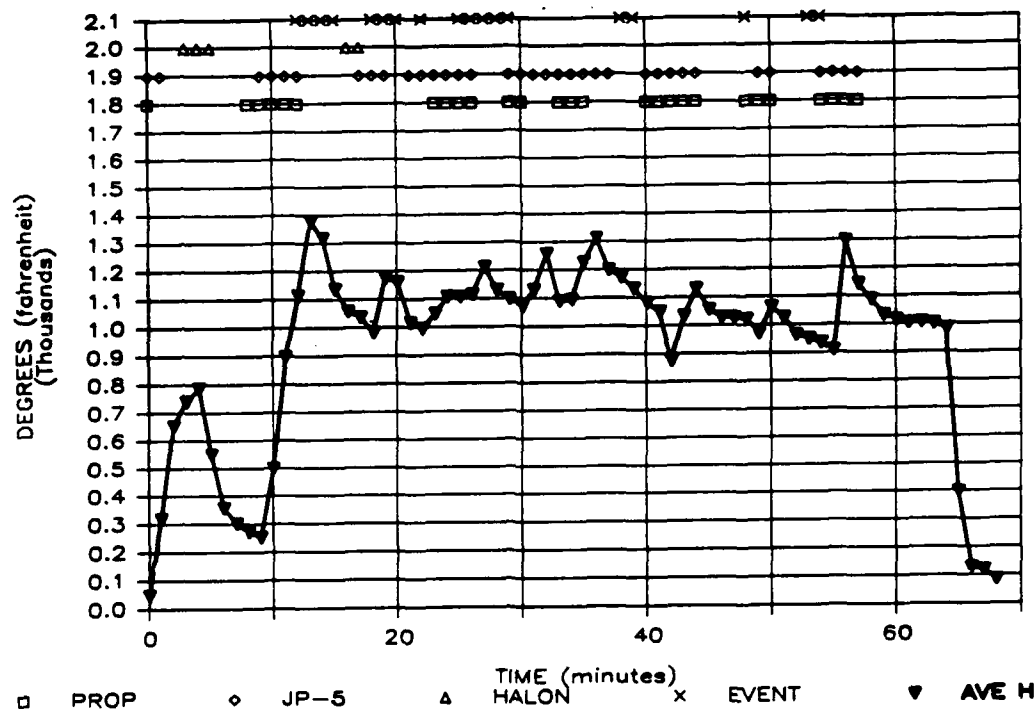
FIGURE 12. Average Temperatures for Horizontal Sonobuoys in Burn 7.

A thermocouple was added to the basket of batteries in burn 7. Figure 13 shows the average temperature until the failure of the thermocouple. Although the thermocouple in the basket measured temperatures as high as 2000°F, cells were observed to continue to vent. It is difficult to conceive how cells could be so close to such a hot source and still not have vented sooner. It should also be noted that the basket of batteries was hotter than the temperatures measured near the sonobuoys, i.e., the blowtorch effect of venting acetonitrile was serving as a source of heat.
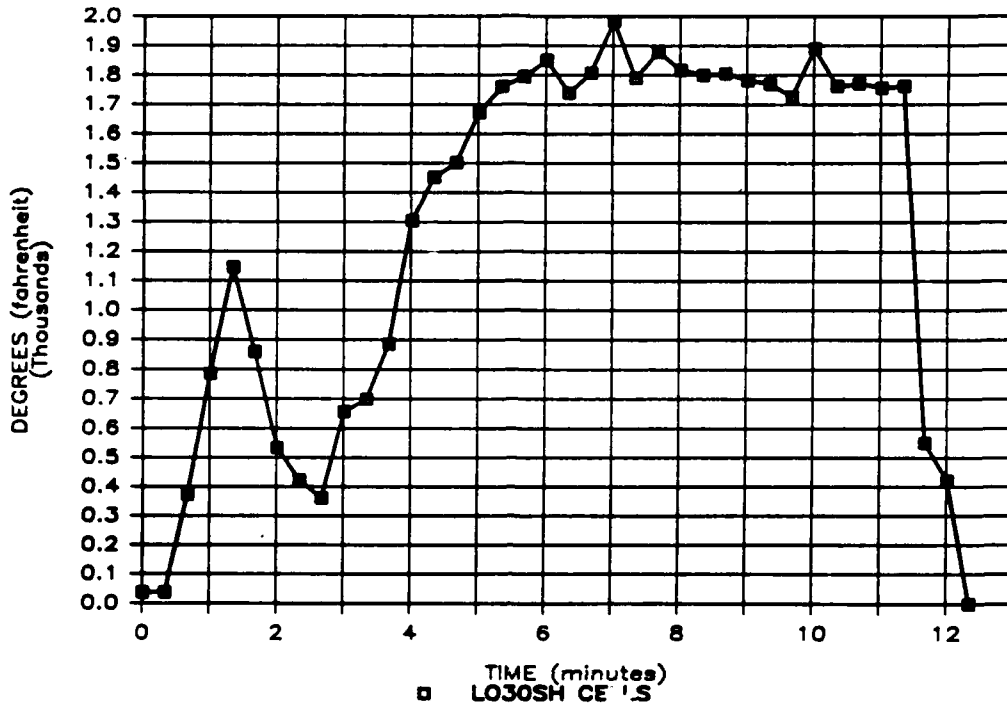
FIGURE 13. Temperature of Basket of Batteries in Burn 7.

BURN 8

Burn 8 was on 8 May 1985 for the purpose of evaluating the effects of carbon dioxide on burning sonobuoys that contain lithium batteries. Figure 14 shows the average temperature near the horizontal sonobuoys while Figure 15 shows the temperature of the basket of batteries. There were no observable reactions of the hot lithium metal with the carbon dioxide applied to the firebox. The carbon dioxide knocked down the flames that were on the front side of the sonobuoys but was ineffective on the sources of flame on the side away from the source of application. Six of the sonobuoys used in burn 8 were Spartan AN/SSQ-62A and two were AN/SSQ-71.
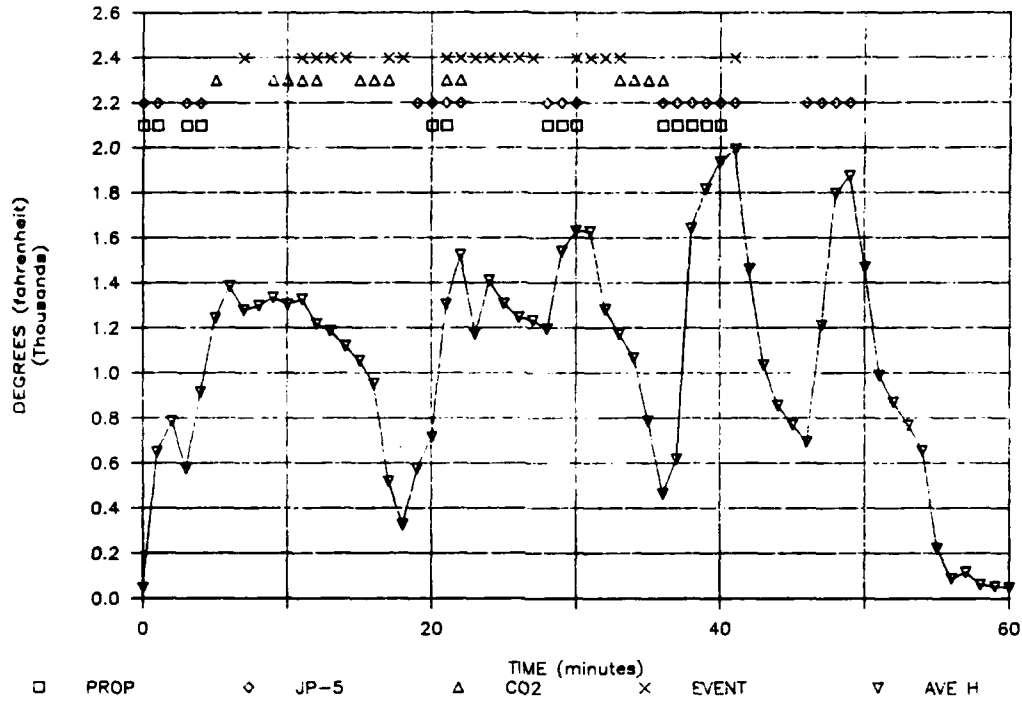
FIGURE 14. Average Temperatures for Horizontal Sonobuoys in Burn 8.
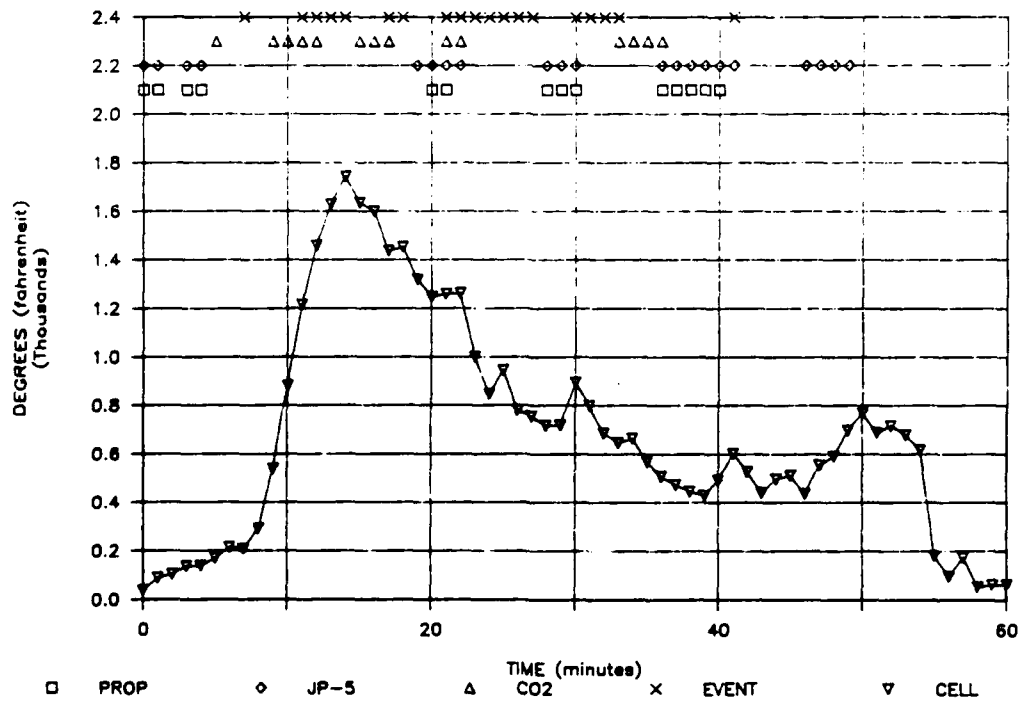
FIGURE 15. Temperature of Basket of Batteries in Burn 8.

BURN 9

Burn 9 on 22 May 1985 used only seven AN/SSQ-62A sonobuoys. Five of these sonobuoys were manufactured by Magnavox Government & Industrial Electronics, Fort Wayne, Ind., while the remaining two were made by Sparton. It should be noted that while it is considered desirable for the extinguishing material to knock down the fire, this was not the primary purpose of these tests. Our primary concern was to determine whether there were any special hazards associated with using lithium batteries with any of the fire-extinguishing agents that would likely be applied to a sonobuoy fire. Figure 16 shows the average temperature near the horizontal sonobuoys, while Figure 17 shows the temperature of the basket of batteries.

Burn 9 used water applied through the extinguishing application system shown in Figure 1. The water was quite effective in extinguishing the sonobuoy fires.
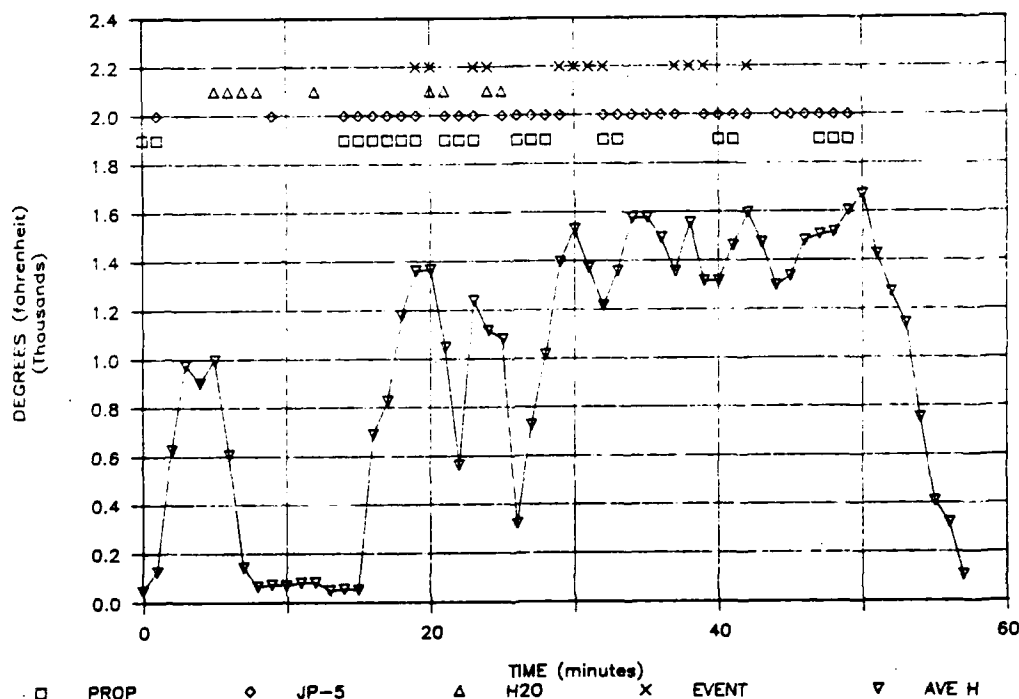
FIGURE 16. Average Temperatures for Horizontal Sonobuoys in Burn 9.
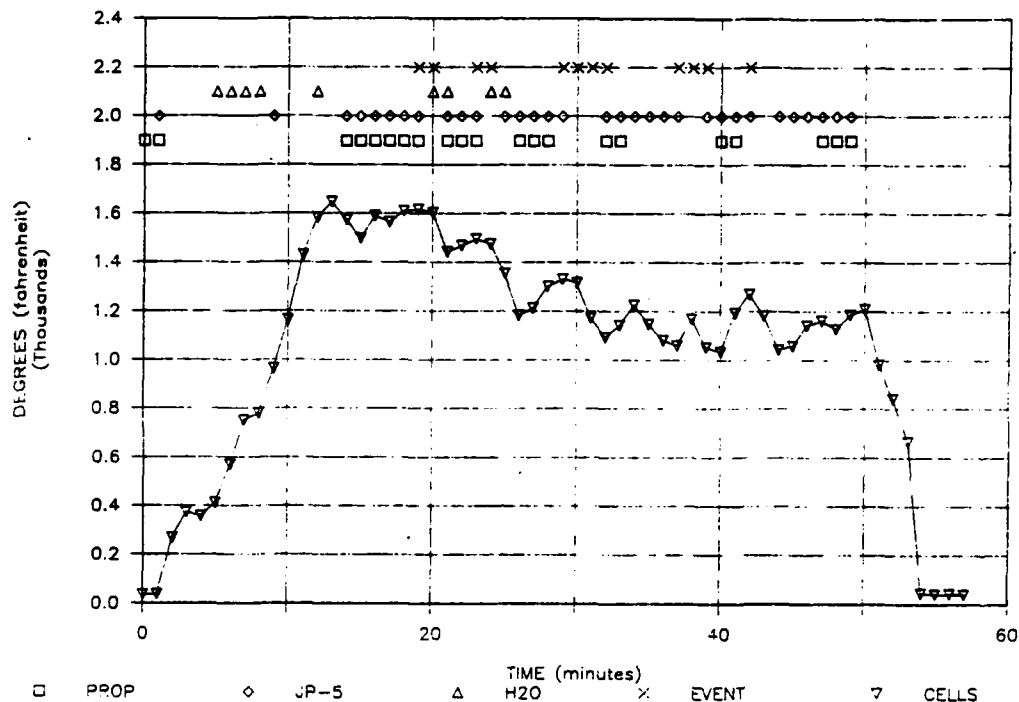
FIGURE 17. Temperatures of Basket of Batteries in Burn 9.

INCINERATED BATTERIES

PHYSICAL EXAMINATION

The incinerated batteries from each test were weighed and examined for holes. Part of this data is presented in Table 1, while some of the findings are indicated in the burns section. This type of data proved to be of much less interest, however, compared to the measurements of the gases released when the opened batteries were placed into water. This information has been submitted for publication in the open literature and is presented in Appendix B.

THE EFFECT OF WATER

We found that up to 6 to 7 liters of gas were released when an opened incinerated Duracell LO-26SN battery was placed into water. The details of our method of measuring the gases are outlined in Appendix B. Table 1 shows the volumes of gas determined for the incinerated

LO-26SH and LO-30SH cells that were tested. The qualitative determination of released gases was performed on a number of instruments. Acetylene was determined on both the Nicolet 7199 Fourier transform infrared (FTIR) spectrometer and the Hewlett-Packard 5985 gas chromatograph/mass spectrometer (GC/MS). For the GC/MS, a 6-foot long by 1/8-inch diameter stainless steel "spherocarb" column (Analabs/Foxboro, New Haven, Conn.) was used to detect methane and a trace of ethylene. The gas chromatographic column was held at 25°C for 2 minutes and raised 5°/min to 200°C. The flow rate was 40 cc/min. Table 2 presents the results of the quantitative analysis that was performed using a Perkin-Elmer Sigma 2000 Gas Chromatograph with a Model 3600 Data Station. The same spherocarb column was used as for the GC/MS. The temperature programming was to hold at 25°C for 4 minutes then increase 20°/minute to 140°C and hold at that temperature for 10.2 minutes. A hot wire detector was used.

TABLE 2. Gas Analysis, Weight, and Volume Measurements.

Percentage is measured by GC.

Test No.	Date tested	Burn No.	Batt., Wt, g	V_{STP}, ℓ[a]	O_2	N_2	H_2	C_2H_2	CH_4	O_2/N_2	H_2/C_2H_2	$CH_4/H_2+C_2H_2$
8	6/12/85	6	46.0	4.52	7.30	25.80	8.20	50.20	...[b]	0.2829	0.1633	0.0000
13	6/14/85	6	47.5	5.60	6.00	21.30	10.90	42.90	...[b]	0.2817	0.2541	0.0000
22	10/15/85	6	38.5	1.73[c]	4.97	18.20	3.92	26.55	1.13	0.2731	0.1476	0.0371
25	10/15/85	6	47.5	4.78	3.06	11.40	11.01	36.02	6.55	0.2684	0.3057	0.1393
27	10/16/85	6	48.0	3.03	4.58	17.08	10.31	28.67	6.53	0.2681	0.3596	0.1675
30	12/10/85	7	47.5	5.77	6.60	23.80	13.30	33.70	5.20	0.2773	0.3947	0.1106
39[d]	12/12/85	7	48.5	5.64	17.20	65.20	0.70	1.60	0.70	0.2638	0.4375	0.3043
42	12/13/85	8	51.0	5.27	6.40	22.90	10.60	45.60	5.70	0.2795	0.2325	0.1014
48	12/16/85	8	37.5	0.93[c]	5.10	18.20	11.10	30.40	5.50	0.2802	0.3651	0.1325
51[d]	12/19/85	8	48.5	6.08	18.10	69.60	6.80	4.00	1.60	0.2601	1.7000	0.1481
54	12/19/85	9	47.0	6.76	5.30	19.00	13.40	39.50	6.00	0.2789	0.3392	0.1134
59	1/16/86	9	37.0	3.00[c]	11.70	43.20	7.90	29.80	3.30	0.2708	0.2651	0.0875
62	1/16/86	9	45.5	2.80	11.30	41.60	7.90	28.10	3.70	0.2716	0.2811	0.1028
65	1/27/86	6	49.0	5.98	6.60	24.00	9.00	23.40	4.30	0.2750	0.3846	0.1327
68	1/27/86	6	47.5	0.98	15.60	57.60	2.10	8.40	1.20	0.2708	0.2500	0.1143
73	1/28/86	6	36.0	1.78[c]	12.60	45.00	9.70	10.90	1.40	0.2800	0.8899	0.0680
79	1/30/86	7	37.5	2.10	12.80	47.20	2.60	26.20	2.40	0.2712	0.0992	0.0833
83	1/31/86	7	48.0	6.62	6.70	24.50	11.50	29.40	6.00	0.2735	0.3912	0.1467
86	2/3/86	7	50.0	2.18	11.80	43.60	5.80	14.80	7.40	0.2706	0.3919	0.3592
89	2/5/86	8	51.5	2.07	14.00	52.40	8.40	14.20	1.90	0.2672	0.5915	0.0841
91	2/6/86	8	50.0	2.70	12.80	45.90	11.40	10.20	6.50	0.2789	1.1176	0.3009
95	2/7/86	8	37.0	2.54[c]	10.40	36.50	10.40	21.40	1.80	0.2849	0.4860	0.0566
96	2/7/86	9	38.5	0.56	16.00	58.90	3.30	0.07	1.10	0.2716	4.7143	0.2750
97	2/7/86	9	49.0	3.33	8.60	30.80	13.20	18.40	6.70	0.2792	0.7174	0.2120
98	2/7/86	9	48.0	4.80	7.20	26.50	12.40	32.40	8.80	0.2717	0.3827	0.1964

[a] Volume standard temperature pressure.
[b] CH_4 was not tested for.
[c] LO-30SH cell.
[d] Helium not used.

As indicated in Appendix B, the presence of sufficient water reactive lithium and lithium carbide to correspond to the initial lithium metal of the anode indicates that most of the lithium remains inside the incinerated batteries. These results are consistent with the failure to observe any reactions between lithium from the batteries and the extinguishing materials. As suggested in Appendix B, when lithium

vapor begins to exit through a small vent, it appears to seal the vent with lithium oxide and nitrides formed through its reaction with the air.

SAFETY CONSIDERATIONS

SULFUR DIOXIDE

Since sulfur dioxide is little affected by the fire and since each cell contains up to 48 grams of it, there is no question that a considerable amount or sulfur dioxide is going to be released into the air if a lithium-sulfur dioxide battery gets hot enough to cause it to vent (above 200°F according to Duracell U.S.A., Bethel, Conn., (Reference 11). Sulfur dioxide is "extremely irritating to eyes and respiratory tract" (Reference 4), and

> "Inhalation of its vapor in concentrations of 8-12 ppm in air causes throat irritation, coughing, constriction of the chest and lacrimation and smarting of the eyes. A concentration of 150 ppm can be endured only a few minutes, due to eye irritation and the effect on the membranes of the nose, throat and lungs. Exposure to a concentration of 500 ppm by volume in air for 30-60 minutes is highly dangerous. Continued exposure to amounts greater than 1000-2000 ppm may be fatal" (Reference 12).

There is sufficient sulfur dioxide in just one LO-26SH cell to fill a 40-foot diameter hemisphere with enough sulfur dioxide to initiate respiratory problems.

Although the fire can initiate the venting of sulfur dioxide, the fire also generates smoke and heat. Since sulfur dioxide is colorless, the smoke from the fire can help to identify the primary direction of its release while heat helps to generate a rapid flow of gases that serves to remove the sulfur dioxide from its point of release, i.e., up into the air. Since sulfur dioxide has a very pungent odor, "the normal person can detect 3-5 ppm by volume in air" (Reference 12). Thus by smell and sight, it may be possible to avoid the respiratory hazards of a venting battery in a fire if one is mobile and has sufficient space to move away from the fire. On the other hand, anyone who has to fight the fire should be wearing a self-contained breathing apparatus since it will not be possible to predict the direction that the smoke will go.

PHYSICAL HAZARDS

Once the carbon dioxide cylinders begin to explode, sonobuoy components can be ejected from the fire. The heaviest item ejected we measured weighed 120 grams (4.2 ounces) that was also thrown the

greatest distance, 19 meters (63 feet). Because of the construction of the sonobuoys, most of this material appears to be ejected from the ends. This was a help in our testing, but would be of little use in the case of a crashed aircraft fire since the positions of the sonobuoys would likely be random and/or unknown to the firefighters. In all likelihood, ordnance from a crashed aircraft could eject material much heavier and further than could the little carbon dioxide cylinders used in sonobuoys.

CONCLUSIONS AND RECOMMENDATIONS

The lithium of a lithium-sulfur dioxide battery such as the Duracell LO-26SH appears to present no problem with respect to the choice of fire-extinguishing materials since most of the lithium remains inside the battery during a fire. It can be a problem, however, if incinerated batteries are exposed to a wet environment for a period of time, as we have found that water can release large quantities of flammable and explosive acetylene, hydrogen, and methane from incinerated lithium batteries.

The sulfur dioxide contained inside a lithium-sulfur dioxide battery, in contrast to the lithium, does present a hazard. It is an eye irritant and will cause difficulties in breathing, even in very low concentrations. In high concentrations, the sulfur dioxide can cause death if it is breathed. The release of sulfur dioxide should be expected at any time during the course of a fire involving lithium-sulfur dioxide containing sonobuoys---even after an hour of burning. Obviously, if one has a choice, self-contained breathing apparatus should be used by anyone close to a fire containing lithium-sulfur dioxide batteries. Acid-type respirators would also be effective for a short period of time but could be overloaded in high concentrations of sulfur dioxide. In the absence of these types of breathing protection devices, it is critical to be upwind and out of the smoke from a fire containing lithium-sulfur dioxide batteries. When very close to the fire at locations free from the smoke and gases of the fire, we measured no sulfur dioxide at times when we detected high concentrations of sulfur dioxide in the combustion gases.

There are some physical hazards associated with the explosion of hot carbon dioxide cylinders used to inflate sonobuoy floats. Face shields and other protective equipment is recommended; however, it is unlikely that the material thrown by the small carbon dioxide cylinders would do much damage to anyone more that 40 feet (12 meters) from the fire. The best defense of a sonobuoy fire is to extinguish it rapidly. On the other hand, if a fire of intact sonobuoys is extinguished within the first 6 to 8 minutes, it is unlikely that the carbon dioxide cylinders and the lithium batteries (if any) will have gotten hot enough to explode. If the sonobuoys have been broken open, on the other hand, the venting may occur within the first minute.

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Although rapid extinguishment of a fire containing lithium-sulfur dioxide batteries solves most of the immediate problems, it may introduce problems in the cleanup of the fire. The shock and crush sensitivity of lithium batteries that have gone through a fire and extinguishment (which can cause rapid cooling) has yet to be determined. Such an investigation is a second phase of this study and will be reported later.

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12. William Braker, Allen L. Mossman, and David Siegel. Effects of Exposure to Toxic Gases, 2nd ed. Lyndhurst, N.J., Matheson, 1979. 172 pp.

Appendix A

TEST PROCEDURE FOR CONFLAGRATION TEST OF
LITHIUM BATTERY CONTAINING SONOBUOYS

Water Extinguishment
Test
7 Jan 1985 revision

TEST PROCEDURE FOR

CONFLAGRATION TEST OF

LITHIUM BATTERY CONTAINING SONOBUOYS

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* Indicates tasks performed by Chemistry Division (Code 385)
  personnel.

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1. PURPOSE AND SCOPE OF TESTS

The purpose of these tests is to determine the reaction of lithium battery containing AN/SSQ-62 sonobuoys when subjected to the intense heat from fire and to observe the advantages and disadvantages of different fire extinguishment agents. The potential for re-ignition of the sonobuoys in the presence of JP-5 fuel is another important consideration. These tests will include gas sampling of the fire plume. It is anticipated that sonobuoys manufactured by different manufacturers may react differently. Follow-on tests will also incorporate the effects of other fire extinguishment agents and perhaps different types of sonobuoys.

The sonobuoys being evaluated are those that contain a number of C-size or larger lithium anode batteries. The AN/SSQ-62 or 62A will contain 12 D-size lithium/sulfur dioxide batteries.

This test procedure is based upon MIL-STD-1648 requirements. This procedure takes precedence over the standard when incompatibilities occur.

2. APPLICABLE DOCUMENTS

2.1 Government Documents

1.	MIL-STD-1648(AS) dated 5 January 1977	Criteria and Test Procedure for Ordnance Exposed to an Aircraft Fuel Fire
2.	NAVSEAINST 9310.1A dated 11 March 1982	Use, Packing, Storage, Transporting and Disposal of Lithium Batteries
3.	NADC Document dated 16 May 1983 by M. Lester, B. Hanson, and LCDR Leland Mills	Safety Procedures Guide for Lithium Sulfur Dioxide Powered Sonobuoys

3. TEST FACILITY AND EQUIPMENT REQUIREMENTS

3.1 To Be Supplied by Test Facility

Item/(Quantity)	Characteristics/Usage
1. Isolated Test Area (1)	Controlled access for hardware item testing.
2. Fuel Burning Fire Box (1)	Minimum 8' x 8' x 10'.
3. JP-5 Fuel and a remotely controlled means to transfer it to spray[a] jets in fire box (1). This will not be the primary fuel.	Sufficient pressure to deliver 10 gallons of fuel within 2 minutes and then shut down with minimal transfer of additional fuel. Up to five gallons of JP-5 will be sprayed onto each sonobuoy PAC (up to 10 gallons in all).

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a. Spray does not mean a mist but rather streams of liquid from small holes.

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Item/(Quantity)	Characteristics/Usage
	This must be activated from the "Fire Control Center". The major supply of JP-5 must be located so that heat and any flying objects from the Fire Box will not cause problems. The JP-5 may be sprayed both before and after fire extinguishment. The JP-5 line should be protected from the heat of the fire and should be drained within 0.5 minutes after shut-off, i.e., so residual JP-5 does not continue to be transferred to the Fire-Box. A water cooled line entering the Fire Box from the 12" center pipe is recommended. A pipe with spray holes standing over the horizontal buoys and a second pipe next to the vertical buoys is suggested. Compressed air could be used to rapidly drain the JP-5 line, copper would be a suitable material for the JP-5 water-cooled line and spray pipes.
4. Fuel Ignition Method remotely controlled (1) (2 would be desirable)	To initiate burn of propane gas. Ignition will be controlled from "Fire Control Center". Ignition device is typically two pieces of metal about an inch apart that are connected to the secondary of a 1 to 200 transformer designed for 110V A.C. primary input.
5. Tank containing about 300 gallons of liquid propane.	Primary fuel for major flame source. The use of a pressure regulator is optional.
6. 1 1/2 inch "black" metal pipe running from the propane storage tank to a 24 V D.C. activated normally closed valve.	One inch line will be needed to connect tank to the 1 1/2 inch pipe. The pipe should be placed so that its uppermost part is at least 4-6 inches underground, and it should be covered with dirt before use. Pipe should meet safety requirements for transfer of propane gas.
7. Box with cover to hold 24 V D.C. activated propane valve. Box should be located about 10' from Fire Box.	Top of box should be just at ground level. Box should allow connection to 24 V D.C. source and entrance of 1 1/2" pipe and exit of 1" pipe.

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Item/(Quantity)	Characteristics/Usage
8. Propane Fire Rake. Located in 8 x 8 x 10' fire box.	Will consist of ten (10) 9-foot-long 1/2-inch black pipes connected to a 1-inch black pipe header. One Hundred burner heads (ordered by Code 3852) will be screwed into the 1/8" NPT threaded holes located nine inches apart on each arm. Diagram shown in Figure 3. Rake will slide into the fire box from the back if it will clear the sonobuoy mounts (this will place more burners underneath the sonobuoys), otherwise slide in from the side (this configuration will result in fewer burners underneath the sonobuoys). Rake will rest on the edge of the 12" high "box" that is normally used to hold the JP-5.
9. Fire Extinguishment system activated from "Fire Control Center". Present test should use water. Follow on tests will use Purple K, Halon 1301 or 1211, and carbon dioxide. Nozzle should be about 6' above ground.	Supplies a spray that will strike primarily inside the fire box at about 125 gallons per minute. Should flood sonobuoys and sides (and back wall) of fire box. Location of nozzle is preferably at center line of sonobuoys. The extinguishment line and the nozzle should be protected from the heat. The nozzle should be firmly mounted so that the activation of the extinguishment material does not move its position. A preliminary test (performed some day prior to the conflagration) should be made to insure that the spray is accurately placed (and to make an approximate measure of the rate of transfer of spray to the fire box as evidenced as how long it takes to fill the fuel chamber of the fire box). The fire box should be free of water on the day of the conflagration test.
10. One inch black pipe line.	One inch line should between 24 V DC controlled valve and connect to the one inch manifold of propane gas rake located in fire box. Most of this line should be beneath the ground in the same manner as the 1 1/2" pipe.

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Item/(Quantity)	Characteristics/Usage
11. Video camera with sound recording capabilities (1). A good sensitive directional microphone should be provided. Microphone should be placed at 6 ± 1 feet above ground level.	For permanent record of battery reactions to fire. With real time indication. Sound amplification should be such that a person talking in front of the fire box in a normal voice can be easily heard with a minimal wind noise in the background. Talking and striking two pieces of metal together should be recorded on video-tape prior to fire ignition.
12. Video Monitor with sound (1).	For real time observation of sonobuoy reactions to fire.
13. Data logger (1) or Strip Chart Recorder (2).	To record continuously or sequentially eleven thermocouples. Scan rate no less than 10 seconds apart 50 to 2,500°F. Real time markers. Two additional channels to record ± 0.5 volts measured to one millivolt for the determination of sulfur dioxide in real time. Ten thousand ohm to 1 magaohm input impedance readout should be expected from the sulfur dioxide amplifier.
14. Control room read-out of results of item 11 above.	Needed to monitor temperature and real time release of sulfur dioxide (with slight time lag for gas flow from burn box to sulfur dioxide sensor.
15. Real Time Clock (1).	For synchronizing video camera and instrumentation events timing.
16. Wind Anemometer and Vane (1)	For measuring wind velocity and direction at test site.
17. Dry and wet bulb thermometer (1 set)	For measuring temperature and humidity at test site.
18. Thermocouples and lead wire (11) (Lengths TBD)	For sensing temperature on and around the battery under test. (0 to 2500°F).
19. Nine switches to activate 110 volt AC circuits carrying 0.5 amps. Switches should be located in blockhouse and the	Switches 1-8 will be used to activate gas sampling solenoids. Switch 9 will be used to, in effect, bring the second sulfur dioxide sensor into the gas flow path.

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Item/(Quantity)	Characteristics/Usage
switchable 0.5 amp at 110V AC power should be available 40-30 feet from the fire box at the gas sampling board.	
20. 110 volt 15 amp circuit, four outlets located at the gas sampling board.	This power will be used to operate the continuous gas flow pump, the high vacuum pump, and test equipment.
21. Shield for gas sampling board-located about 40 feet from fire box (but not between fire box and TV camera). Shield for propane tank (two shields total).	Provide protection, heat-wise and projectile-wise at gas sampling board and propane tank.
22. Stand to hold overhead gas sampling line (1)	Provide support for gas sampling line.
23. Cooling water, on order of five gallons per minute. Brackish water would be fine. Connect to 1/2" O.D. tubing. Also cooling water for JP-5 line (2).	Needed to cool gas sampling line above box and JP-5 line coming from center-pipe in fire box.
24. Sonobuoys (8)	Should all be the same AN/SSQ type, be from the same Mfr, (Sparton has 2 #'s 82268 and 56118) and preferably the same NALC number.

3.2 Test Facility

Because of the hazardous nature of the test, the test facility will be located in an area remote from other activities and thoroughfares. Preferably it will be separated from them by hills as well as distance. Also a power source (115VAC, single phase and 24 V DC) preferably inside an instrumentation room or blockhouse will be required to supply power to and house the instrumentation. The instrumentation should be located as near as possible to the holding fixture to minimize the thermocouple lead lengths. Metal panel or other type safety barriers between the test fixture and instrumentation should be used if necessary. The ground 15 feet in front of the fire box should be raked clean of all debris and photographed sometime prior to the ignition of the fuel and the next day before removal of spent batteries and CO_2 cylinders.

3.3 Test Equipment

3.3.1 Test Equipment Set-Up

Figure 1. depicts the test set-up for the fuel fire test. The horizontal

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and vertical PACS of 4 buoys each will be placed at or above top line of front baffle on Fire Box on each side of Center Pipe. The directional sound transducer should be located at about the same height as the center of the vertical buoy PAC. The gas sampling board should be located 40 feet from the fire box at a position out of line of sight of the front of the fire box. It is recommended that the gas sampling board be located on the west side of the fire box. (see Figure 2). The water cooled gas sampling probe shall be installed, centered on the west side of the fire box. After the buoys have been mounted the cooling water shall be turned on prior to fuel ignition.

4. TEST PREPARATIONS

4.1 Battery Safety Precautions

4.1.1. General

WARNING

Lithium-Sulfur Dioxide battery used in the test sonobuoys is designed to vent if high internal pressures occur due to high temperatures caused by internal malfunctions or external environments. The acid gases and vapors vented are corrosive and toxic and can cause acute systemic effects if inhaled or absorbed into the skin. If water reaches the lithium, an explosive reaction will occur which will amplify the hazards. All personnel associated with this test should become familiar with the safety procedures and precautions described in this procedure, plus those referenced in the Applicable Documents, paragraph 2, of this procedure.

4.1.2 Buoy Considerations

1. Each buoy contains up to three pressurized CO_2 cylinders which can generate high velocity "shrapnel-like" pieces of metal.

2. If the wind shifts so as to blow in the direction of the fire control block-house, personnel may have to evacuate if SO_2 is still being released from the batteries. It is very unlikely that this will occur because of the up-draft of the fire, i.e., a cloud going just "over" the blockhouse should cause no problem to anyone in the blockhouse. Only if the wind were to blow very hard so that fumes would not have a chance to rise, would this be a problem. The test should not be initiated in such a wind.

4.2 Test Conditions

The test will be performed on a non-rainy day to eliminate water cooling effects on the test article and in the fuel from influencing the test results. The winds will be no more than 5 mph for the same reason and in a direction away from the instrumentation and personnel fall-back areas. Measurements of temperature (dry and wet bulb), wind velocity and direction will be made immediately before and after the test. Major changes in wind direction and/or velocity should be recorded and included in the test report.

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4.3 Test Instrumentation and Equipment .

4.3.1 Thermocouples

Temperature inside the PAC of 4 buoys and the temperature of the air around the buoys will be measured during the test either continuously or periodically at a rate of no less than 10 seconds per complete scan cycle. The temperature will be sensed by appropriate thermocouples suitably insulated from the heat from the fuel fire and connected by lead wires to a data logger or multi-channel strip chart recorders. Temperatures in the 1500 to 2500°F range are expected. Three thermocouples will monitor the temperature of the buoy PAC (see Figure 1). Two other thermocouples will be mounted six inches from the PAC. An eleventh thermocouple will be connected to the fire box so as to measure the temperature of one of its sides.

4.3.2 Camera and Photographic Coverage

A closed circuit color video camera shall be used to monitor each test. Sound should be recorded. A video and sound monitor should be provided. Still photos should be taken of the test set up before and after the test. In particular, official photographs of the ground in front of the fire box should be taken before and after to note anything ejected from the fire box. Send three copies of the prints, viewgraphs and negatives (unless filed) along with a copy of the video to Dr. Aaron Fletcher, Code 3852 within 10 days of the test. A second set should be sent to Hardy Tyson, Code 3383. Video coverage of EOD clean-up should be performed.

4.3.3 Real Time Synchronization

The camera, strip chart recorders and/or data logger will be supplied with a common time base for use in subsequent analysis of battery reactions.

4.4 Instrumentation Checkout

The thermocouple instrumentation will be installed and checked out after mounting the buoys.

4.5 Transportation of Battery to Test Site

Transportation of the buoys will be in accordance with the instructions of Part 2. of this test plan.

4.6 Mounting the Buoys

See Figure 1. Two PACS of 4 buoys each will be mounted with their lowest portions on line with the Front Baffle of the Fire Box. They should be located on each side of the Center Instrument Pipe, 4' into the Fire Box as measured from the front plane.

5. TEST PROCEDURES

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5.1 Instrumentation and Auxillary Equipment Start-Up

Prior to igniting the fuel, the instrumentation and camera units will be energized and reference measurements of air temperature (dry and wet bulb), and wind velocity and direction taken. All personnel will be in the prescribed test fall-back/observation area, prior to igniting the fuel. Just prior to fuel ignition, the vacuum pump on the gas sampling board should be made "ready".* All cooling water should be turned on and manual valves preceeding electrically controlled valves should be opened.

5.2 Fuel Ignition

At the direction of the test conductor, the propane igniter will be turned on followed by turning on the propane fuel switch.

5.3 Fuel Burn Phases

The test conductor will record the time of the propane fire ignition. There will be more than one propane fuel burn phase. Temperature and voltage instrumentation will be monitored and the test conductor will ensure that the timing is appropriately recorded or annotated on the recorders. Particular attention shall be paid to monitoring the test set-up by sight, and by sound and by instrumentation looking for any signs of battery reactions such as venting. When venting is observed, one of the eight gas sample bottle switches may be activated for 20 ± 2 seconds at the discretion of gas sampling operator*. The time should be noted for the activation of the gas sample bottle switches or switch #9, the introduction of the 2nd sulfur dioxide sensor. The flame may become red if the lithium from the battery is vented. A Code 3852 representative shall indicate the time to turn on or off the propane fuel (with concurance of the firing officer.

5.4 JP-5 Addition Phases - Only the 2nd addition phase will be performed using water as the extinguishment material.

Just prior to the initiation of the application of the fire extinguishment agent, 2-5 gallons of JP-5 will be transferred to each of the two buoy PACS within a 2 minute period. There will be at least four JP-5 addition phases. (Two with propane burning and two after fire is extinguished). It is the intention to add enough JP-5 onto the sonobuoys so that a major portion of the flame originating from the sonobuoys is caused by the JP-5. Thus, it is desirable to wet-down a major portion of the sonobuoys (and the pan the buoys are sitting on), but not so much so as to cause a major reduction in the effects of the burning of the sonobuoy components.

JP-5 will also be added after the fire is extinguished so as to see whether the sonobuoys can be re-ignited by a (simulated) second fuel spillage. This second addition should be about 1-2 gallons. The time of this fire-extinguished addition and the addition with propane still burning will be initiated by a Code 3852 person with concurance of the Firing Officer. These times will be recorded* and included in the test report.

5.5 Propane Shut-Off Phase

After the addition of the JP-5 (probably within 30 seconds), the propane

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electrically controlled valve will be closed so that the propane fuel will
be turned off. These times will be recorded* and reported in the test report.

5.6 Extinguishment Phases

Within seconds after the propane has been shut off the application of
the fire extinguishment material will be initiated from the "Fire Control
Center". The decision as to when the fire extinguishment material is turned
off will be made by a Code 3852 representative with concurance of the firing
officer. The firing officer has the final authority and decision for this
fire extinguishment stage. The time the extinguishment is concluded will be
recorded* and reported in the test report.

5.7 Addition of JP-5 to Extinguished Buoys

As covered in section 5.4

5.8 Re-ignition of Propane

The electrical fire ignition service will be turned on followed by
opening the propane electrically controlled valve. It is likely that
the re-ignition may not be a smooth operation as the propane burner heads
will have different amounts of fire extinguishment material on them.

5.9 2nd JP-5 addition, Propane Shut-Off, and Extinguishment

Steps 5.4, 5.5, 5.6, 5.7 and 5.8 will be repeated a 2nd time. This
will likely occur about 1 minute after the initiation of the loud reports
assuming that the first sequence occurs within the first 8-10 minutes of
the burn. The time for the 2nd sequence will initiated by the Code 3852
representative with concurance of the firing officer.

5.10 Final Propane Burn

Ten minutes after the last "report", or sound of venting, the propane
electrically controlled valve may be shut off. This may require as much
as 50 minutes of total propane burning.

5.11 Cool-Down Phase, initial

After the fire has burned out, the instrumentation equipment will remain
on and monitored until all functioning thermocouples indicate a temperature
below 400°F or after 1.5 hrs after the propane has stopped burning, whichever
is LATER. i.e. the initial cool down phase is in effect for at least 1.5 hrs
after the propane has been turned off and longer if the thermocouples are still
above 400°F at the end of 1.5 hrs. Personnel will remain in the fall-back
area throughout this period. The test conductor will note and announce the
end of the initial cool-down period based upon the time after burn-out and
temperature instrumentation. If a failure in the instrumentation has occur-
red, a minimum period of two hours must elapse before the initial cool-down
is declared ended. At the end of the initial cool-down phase, one person*
(and a safety back-up who normally remains 100 ft from fire box), will attend

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to gas sampling board. The cooling water and manual valves (such as associated with the propane tanks) should be turned off at the end of the initial cool-down phase.

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WARNING

The end of the initial cool-down period DOES NOT MEAN that it is considered
safe to approach the FRONT of the fire box closer than 100 feet.  The initial
cool-down period is considered long enough that heat-radiation from the walls
of the fire-box will be negligible and that there will be a negligible probability
of a "heat protected" battery from venting and producing an unavoidable vapor
hazard greater than 40 feet from the sides or back of the fire box, i.e. at
the gas sampling board.  As an extra precaution, personnel approaching closer
than within 75 feet of the burn box, following the initial cool down but before
the final cool down phase, are advised to have an acid gas respirator available.
A safety stand-by person equipped with an acid gas respirator should remain
(unless needed) at least 100 feet from the fire box.  This safety stand-by
person should be available to help the person collecting the gas sample bottles
at the end of the initial cool-down period in the event of any accident.
During the collection of the gas sample bottles, the TV camera should be
directed to view the gas sample board area so that outside emergency assist-
ance can be requested in the event that it is needed.  If any odor of sulfur
dioxide is detected, personnel should not enter the area (any personnel
working near fire-box should be given the opportunity to smell a test sample
of $SO_2$).  If the odor occurs once in the area, personnel should leave the
area for at least 15 minutes.  In the case of a strong odor, personnel with
acid gas respirators should use their respirator until 150 feet upwind (or
at least not down wind) from the fire box.
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5.12 Cool-Down Phase, Final

Twelve hours after the fuel burn-out should allow sufficient time for any slow "fire-protected", slow-venting, batteries to have vented. It is also of sufficient time for "temperature-change" effects to have occured on "fire-protected" batteries. Any time after the end of the final cool-down phase, photographs or video camera coverage may be taken.

5.13 Documentation; after Final Cool-down

Photographs should be taken of the remains of the sonobuoys that were in the vertical and horizontal configurations. In addition, photographs (with a ruler placed for relative size) should be made of any holes in the screen under the buoys. The location of such holes should be recorded. Similarly, photographs should be taken of the ground in front of the fire box. Any objects (other than scale from the fire box, itself) ejected from the fire box should have their positions relative to the front of the fire box measured and the object tagged (by EOD if object is a battery), and identified to whatever extent is feasable for the above photographs. An identifying label located in the view of the camera should be used to show the date and nature of the test i.e. Sonobuoy Burn, xx August 1984. All holes in the screen should be repaired before the next test.

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5.14 Explosive Ordnance Disposal (EOD)

Combined batteries and CO_2 cartridges from each of the two sonobuoy configurations should be collected separately. Batteries and CO_2 cartridges that are located some distance from the horizontal buoys (on left facing fire box) or on vertical buoys (on right) should be included in a third collection for "unknown". These three collections of batteries and CO_2 cartridges from the two configurations and the unknowns along with any taged objects found in front of the fire box should be held at EOD for three weeks for further post-mortem tests by Code 3852. Code 3852 (extention 1629 or 1646) should be notified by EOD as to when these items would be available. Video coverage of EOD clean-up should be performed.

5.15 Buoy and Battery Removal and Disposition

Two possible battery reaction scenarios exist during or following the burn period which determine how the batteries are to be handled following the cool-down period:

Case A. Battery vented during the fire or cool-down phases.
Case B. No positive evidence of battery vented was noted.

Case A presents the least hazard particularly if the venting occurred during the fire period since it is most likely that all the chemical reactions have been completed, their vapors expelled, and the remaining residues relativley inert. These buoy remains should be disposed of into a controlled land fill. The remains of the vented batteries could contain a caustic residue.

In Case B, heated, unvented, intact batteries represent a serious safety hazard and should be treated as an o..Jnance device. The battery should not be approached for a period of 12 hours after fuel burn-out. During this period, controlled access to the test site should be maintained to prevent personnel from inadvertently being exposed to the battery hazards. EOD should be called to remove the intact battery, being prepared for the breathing and eye hazards as well as the explosive hazards (see Part 2), i.e., they should wear flak vests, heavy gloves, and full face shields as a minimum. If there is any suggestions to indicate that a battery is intact (such as might be the case for a battery outside the fire box), an acid gas face mask should be worn in addition to the use of a flak vest and heavy gloves. These recommendations should not preclude other protective measures that the EOD members would employ in working with explosive materials.

Since it is not known, in advance, whether Case A or Case B conditions will be in effect, the EOD personnel (a minumum of two is recommended) should consider that Case B conditions exist.

5.16 Recommended Procedures for Test Deviations

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5.16.1 Failure to Turn On or Ignite Propane after Initial Burn

If the sonobuoys have not reached the end of the "Final Propane Burn" (section 5.10), and it is not possible to re-ignite the propane, the test should proceed to the "Initial Cool-Down-Phase". Manual valves to the propane (and JP-5) should be closed, gas sample valves closed (if samples had been taken). The next day, the Propane Rake should be removed from the fire box taking care not to approach the front of the fire box. The test should now continue following the 1 August 1984 test procedure using JP-5 as the primary fuel. If there is a strong odor of sulfur dioxide, it will be necessary to wear an acid gas respirator during removal of the Propane Rake and the preparations for the JP-5 fuel fire.

5.16.2 Failure to Turn On JP-5

Test should proceed without JP-5 addition.

5.16.2 Failure to Turn Off JP-5

Firing officer should assign someone to turn off manual valve of JP-5 tank. This individual should be qualified to use an Acid Type Respirator and should wear respirator when about 200 feet from fire box. Approach to JP-5 valve should be out of direct line of front of fire box if closer than 100 feet from fire box unless behind the protective shield.

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6.0 REPORTING PROCEDURE

6.1 As soon as practical, after completion of this test, the person
who conducted it, or the cognizant firing officer, shall write a test
report. This report must be delivered in a timely manner to A. N.
Fletcher, Code 3852.

6.2 The test report supplied by Code 3384 shall include, as a
minimum, but not be limited to the following:

   1. Any major deviations from the test plan setup.

   2. A chronological summary of the significant events occurring
   during the test.

   3. A tabulation of the meaningful data extracted from the test
   i.e. the data logger print out. Copies of all data extracted
   shall be enclosed with the test report in addition to this tab-
   ulation.

   4. 8"x10" photographs, negatives, view graphs and copy of
   video tape. A second set photographs and video tape shall be
   sent to Hardy Tyson, Code 3383. See section 4.3.2 for more
   complete data.

   5. Description of Sonobuoys used in test (Form 6.4).

   6. Completion of Form 6.3 and 6.4.

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6.3 DATA SHEET FOR LITHIUM BATTERY
SONOBUOY CONFLAGRATION TEST

TEST DATE:_____

THERMOCOUPLE AND SO_2 PROBE POSITIONS

Data Logger   Fig. 1. Designation

GAS SAMPLING BOARD

Switch #	Time activated Hr/Min/Sec

T/C #1_____#1

T/C #2_____#2

T/C #3_____#3   1_____

T/C #4_____#4   2_____

T/C #5_____#5   3_____

T/C #6_____#1'   4_____

T/C #7_____#2'   5_____

T/C #8_____#3'   6_____

T/C #9_____#4'   7_____

T/C #10_____#5'   8_____

T/C #11_____Fire Box   9_____

E-1 #12 Sulfur dioxide electrode (#1)

E-2 #13 Sulfur dioxide electrode (#2)

	Before Test	After Fuel Burn-out
TEMPERATURE (DRY BULB):	_____°F, _____HRS.;	_____°F. _____HRS.
TEMPERATURE (WET BULB):	_____°F, _____HRS.;	_____°F. _____HRS.
WIND VELOCITY (KNOTS):	_____ , _____HRS.;	_____ , _____HRS.
WIND DIRECTION (FROM):	_____, ____"____HRS.;	_____, ____"____HRS.

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6.4 TIME SEQUENCE

Date of Test _____

Actual Time   Time from Initiation of Test

Propane ignition _____

JP-5 turned on _____

JP-5 turned off _____

Propane turned off _____

Extinguishment turned on _____

Extinguishment turned off _____

JP-5 turned on _____ Not performed for water extinguishment _____

JP-5 turned off _____ Not performed for water extinguishment _____

Propane turned on _____

JP-5 turned on _____

JP-5 turned off _____

Propane turned off _____

Extinguishment turned on _____

Extinguishment turned off _____

JP-5 turned on _____

JP-5 turned off _____

Propane turned on _____

Propane turned off _____

End of initial cool down phase _____

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6.5   SONOBUOY IDENTIFICATION

Sonobuoy   AN/SSQ_____   NALC # 8W_____

                                                  (if all the same)

Manufacturer's Code Number_____or_____.

Typical Contract Number__N000_____ - year #___-_____-_____

Are all contract numbers the same? yes/no. If not, include below.

| Horizontal Buoys | Vertical Buoys |

1. Year #_____ NALC # 8W_____   1'. Year #_____ NALC # 8W_____
    B_____   LOT_____   B_____   LOT_____
    SLC yes/no Contract #_____   SLC yes/no Contract #_____

2. Year #_____ NALC # 8W_____   2'. Year #_____ NALC # 8W_____
    B_____   LOT_____   B_____   LOT_____
    SLC yes/no Contract #_____   SLC yes/no Contract #_____

3. Year #_____ NALC 8W_____   3'. Year #_____ NALC # 8W_____
    B_____   LOT_____   B_____   LOT_____
    SLC yes/no Contract #_____   SLC yes/no Contract #_____

4. Year #_____ NALC # 8W_____   4'. Year #_____ NALC # 8W_____
    B_____   LOT_____   B_____   LOT_____
    SLC yes/no Contract #____·____   SLC yes/no Contract #_____

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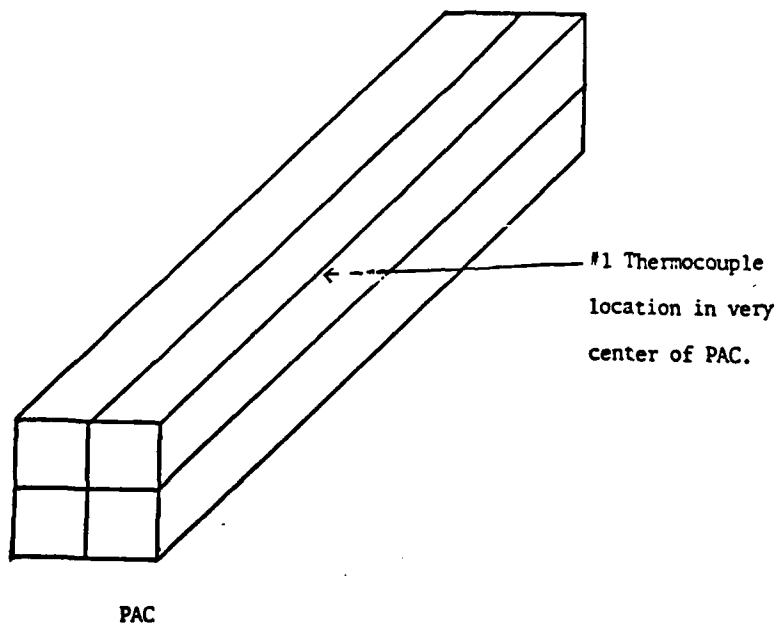|		6.6 DAILY LOG AND REMARKS
DATE	HOUR	EVENT/REMARKS

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FIGURE 1a. Location of Thermocouples

5 Thermocouples per PAC

    #1 in center of PAC

    #2 between support and PAC

    #3 opposite #2 on top of PAC

    #4 centerline about 4" to 8" from PAC

    #5 centerline about 4" to 8" from PAC

#1 Thermocouple location in very center of PAC.

PAC

- FIGURE 1b. Locations of PACS and Thermocouples

Steel Straps (2) to hold PAC together placed ¼ length from each end. Rod or steel strip to hold PAC in place between PAC and strap OK.

One PAC to stand vertical in small steel pan or on plate.
One PAC to lay horizontal in steel pan or on plate.
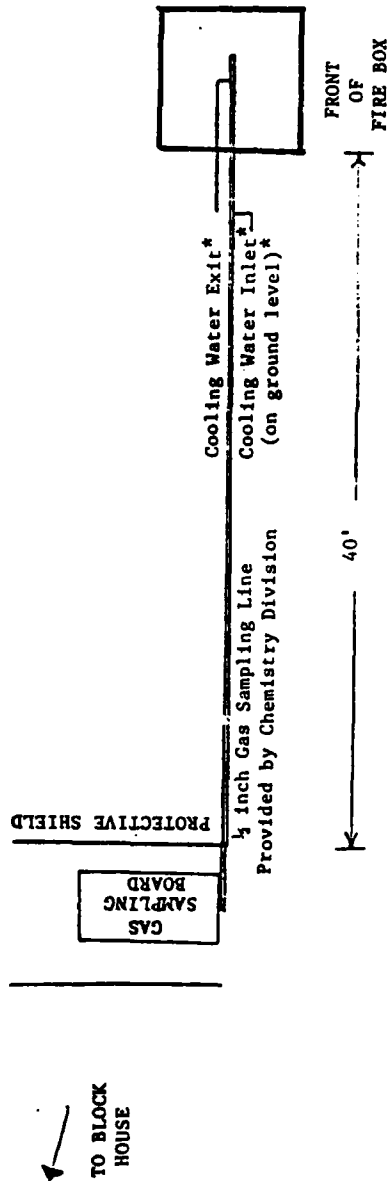Wire mesh placed under pan supports.
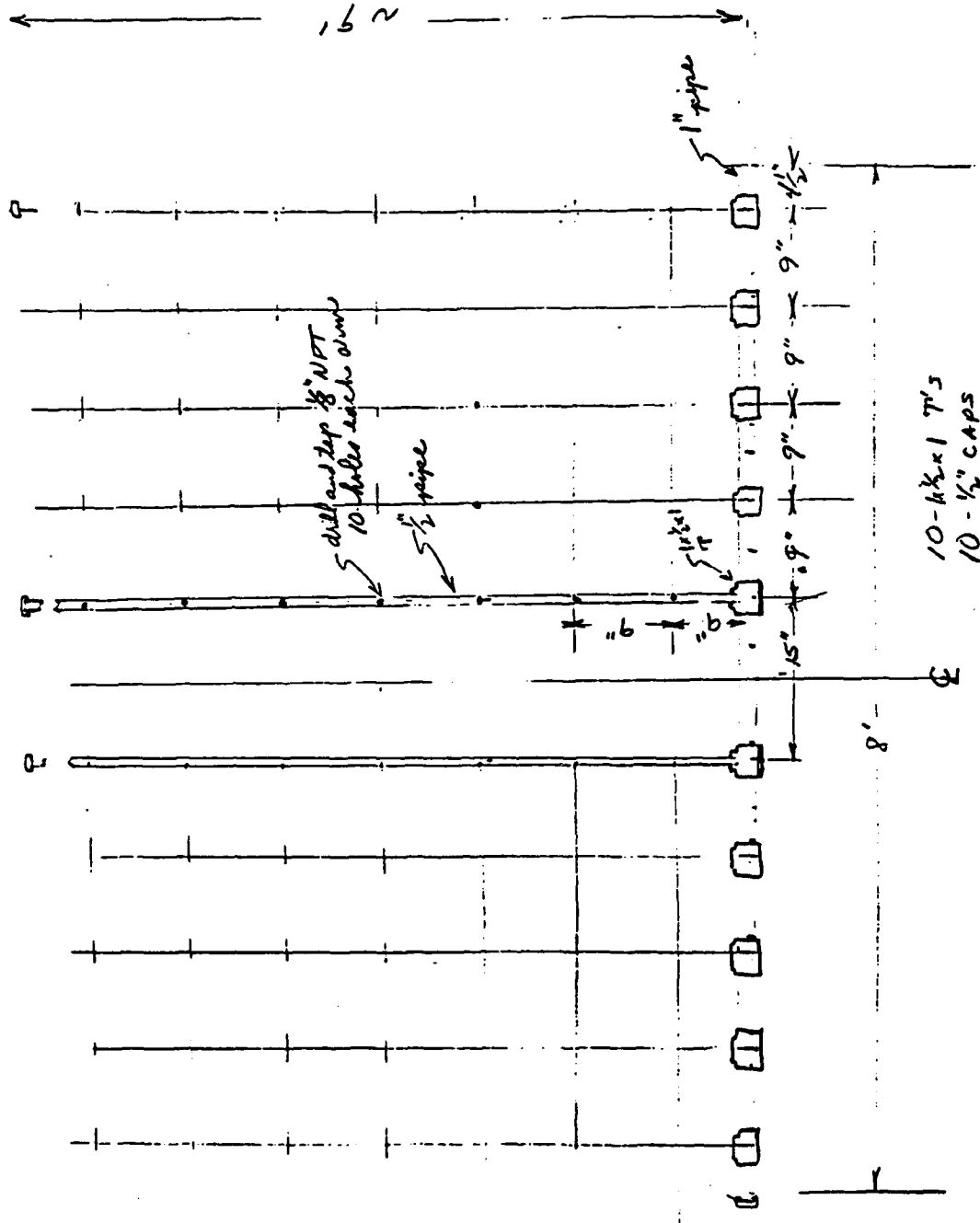

Thermocouple #2 between support and PAC Thermocouple #2' between support and PAC

Wire mesh
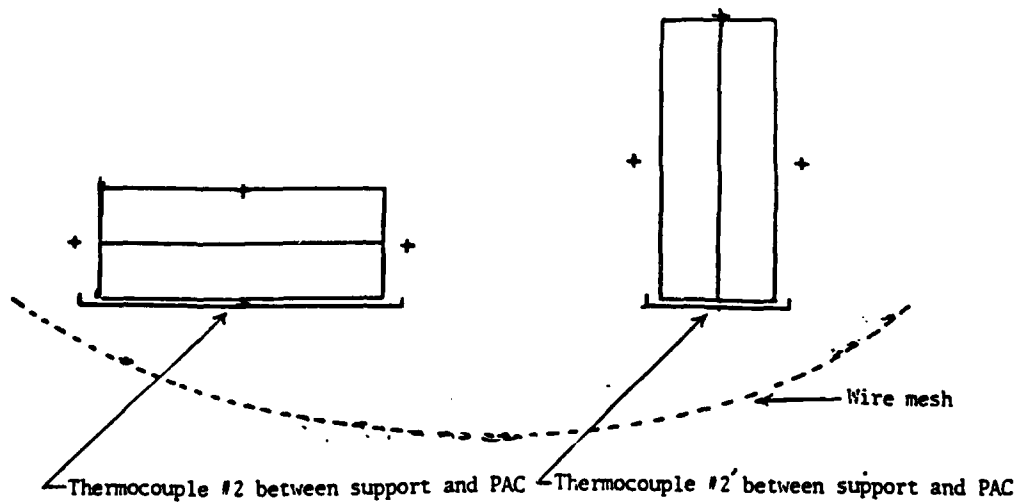
FIGURE 2. LAYOUT OF TEST SITE

FIGURE 3. PROPANE GAS RAKE

Appendix B

THE EFFECT OF WATER ON INCINERATED
LITHIUM-SULFUR DIOXIDE BATTERIES

THE EFFECT OF WATER ON INCINERATED LITHIUM–SULFUR DIOXIDE BATTERIES

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Summary

Incinerated lithium batteries were found to release enough gases upon the addition of water to account for all of the lithium of the anode and part of the aluminium used in the cathode collector, *i.e.*, most of the lithium was not released from the cells upon incineration. The major gas released was found to be acetylene indicating that a portion of the lithium had reacted with carbon from the cathode and formed lithium carbide.

Introduction

What happens to the lithium metal of an electrochemical cell involved in a fire ? We have often measured temperatures as high as 1090 °C in our fire-box using JP-5 as a fuel. At these temperatures lithium metal has a reported vapor pressure of 100 Torr [1] and could consequently be expected to rapidly escape from the cell. The results from this study indicate that this is not the case since the lithium reacts with cell components forming water reactive materials. In addition, the battery vents appear to be plugged with the products formed from the reactions of lithium with oxygen and nitrogen, so that lithium is often sealed inside cells that have previously vented their more volatile components.

Experimental

We measured the volume and nature of the gases released from water-soaked Duracell L0-26SH and L0-30SH cells that had been incinerated for periods of 30 - 60 min at firebox temperatures averaging 1000 °C. Both propane gas and JP-5 were used as sources of fuel to heat the firebox. Water was used to quickly cool the firebox at the conclusion of a burn. The

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batteries were placed in plastic bags for storage on the following day.

Just prior to testing, one end of each cell was cut off with a tubing cutter. Up to 3% of the cells showed evidence of air-reactive, glowing granules at this point. Each cell was then placed into an air-tight container and sufficient water was slowly added so as to allow complete reaction. The volumes of gases released were measured by a series of inverted cylinders filled with water. The pressures of these volumes were corrected for the height of water remaining in the cylinders. The volume was converted to the standard temperature and pressure (STP) of one atmosphere at 0 °C. Corrections were not made for the amount of gases dissolved in the water, so the resulting volumes represent minimum values. For ease of analysis, the apparatus was often preflushed with helium prior to the addition of water. The nominal weight of the incinerated L0-26SH cells was 47 g and that of the L0-30SH cells was 37 g. Some of these cells already had large holes in their sides and most of their "vents" appeared to have resealed (by products of air-reactive lithium vapor?).

Figure 1 shows the volume of gases measured from the L0-26SH cells. The smaller L0-30SH cells produced proportionately smaller volumes. We have analyzed the gases evolved from the reaction of water with the contents of 25 Duracell L0-26SH and L0-30SH cells. The results of the tests using gas chromatography (GC) are shown in Table 1. We detected primarily acetylene,
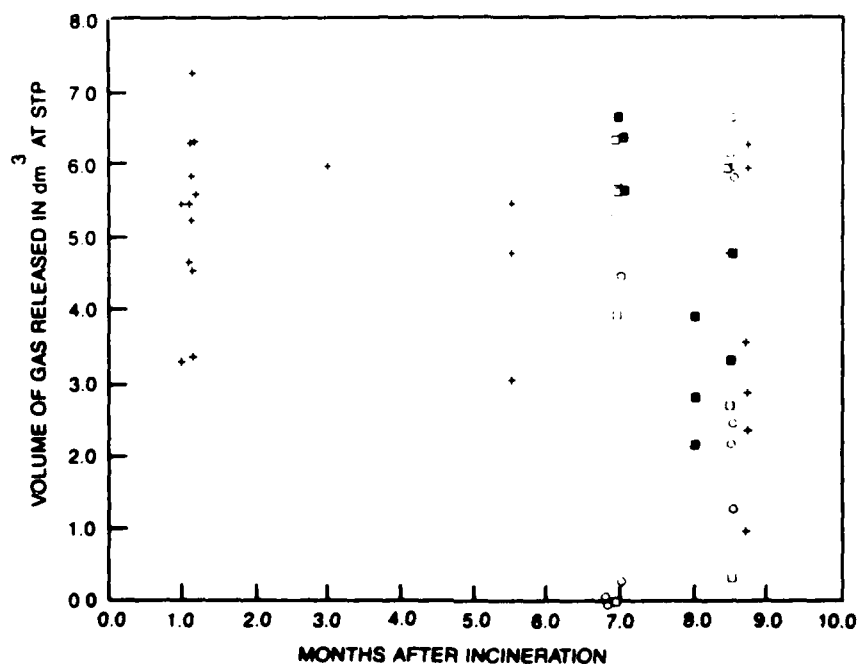

Fig. 1. Volume of gas released from water-soaked incinerated Duracell L0-26SH cells after storage for various periods of time. Different symbols indicate different burns.

TABLE 1

Gas analysis, weight, and volume measurements

| Test no. | Date tested | Burn no. | Batt. wt. (g) | Vol.STP (l)[a] | Percentage measured by GC | | | | | O_2/N_2 | H_2/C_2H_2 | $CH_4/H_2+C_2H_2$ |
					O_2 (%)	N_2 (%)	H_2 (%)	C_2H_2 (%)	CH_4 (%)			
8	6/12/85	6	46.0	4.52	7.30	25.80	8.20	50.20	...[b]	0.2829	0.1633	0.0000
13	6/14/85	6	47.5	5.60	6.00	21.30	10.90	42.90	...[b]	0.2817	0.2541	0.0000
22	10/15/85	6	38.5	1.73[c]	4.97	18.20	3.92	26.55	1.13	0.2731	0.1476	0.0371
25	10/15/85	6	47.5	4.78	3.06	11.40	11.01	36.02	6.55	0.2684	0.3057	0.1393
27	10/16/85	6	48.0	3.03	4.58	17.08	10.31	28.67	6.53	0.2681	0.3596	0.1675
30	12/10/85	7	47.5	5.77	6.60	23.80	13.30	33.70	5.20	0.2773	0.3947	0.1106
39[d]	12/12/85	7	48.5	5.64	17.20	65.20	0.70	1.60	0.70	0.2638	0.4375	0.3043
42	12/13/85	8	51.0	5.27	6.40	22.90	10.60	45.60	5.70	0.2795	0.2325	0.1014
48	12/16/85	8	37.5	0.93[c]	5.10	18.20	11.10	30.40	5.50	0.2802	0.3651	0.1325
51[d]	12/19/85	8	48.5	6.08	18.10	69.60	6.80	4.00	1.60	0.2601	1.7000	0.1481
54	12/19/85	9	47.0	6.76	5.30	19.00	13.40	39.50	6.00	0.2789	0.3392	0.1134
59	1/16/86	9	37.0	3.00[c]	11.70	43.20	7.90	29.80	3.30	0.2708	0.2651	0.0875
62	1/16/86	9	45.5	2.80	11.30	41.60	7.90	28.10	3.70	0.2716	0.2811	0.1028
65	1/27/86	6	49.0	5.98	6.60	24.00	9.00	23.40	4.30	0.2750	0.3846	0.1327
68	1/27/86	6	47.5	0.98	15.60	57.60	2.10	8.40	1.20	0.2708	0.2500	0.1143
73	1/28/86	6	36.0	1.78[c]	12.60	45.00	9.70	10.90	1.40	0.2800	0.8899	0.0680
79	1/30/86	7	37.5	2.10[c]	12.80	47.20	2.60	26.20	2.40	0.2712	0.0992	0.0833
83	1/31/86	7	48.0	6.62	6.70	24.50	11.50	29.40	6.00	0.2735	0.3912	0.1467
86	2/ 3/86	7	50.0	2.18	11.80	43.60	5.80	14.80	7.40	0.2706	0.3919	0.3592
89	2/ 5/86	8	51.5	2.07	14.00	52.40	8.40	14.20	1.90	0.2672	0.5915	0.0841
91	2/ 6/86	8	50.0	2.70	12.80	45.90	11.40	10.20	6.50	0.2789	1.1176	0.3009
95	2/ 7/86	8	37.0	2.54[c]	10.40	36.50	10.40	21.40	1.80	0.2849	0.4860	0.0566
96	2/ 7/86	9	38.5	0.56[c]	16.00	58.90	3.30	0.07	1.10	0.2716	4.7143	0.2750
97	2/ 7/86	9	49.0	3.33	8.60	30.80	13.20	18.40	6.70	0.2792	0.7174	0.2120
98	2/ 7/86	9	48.0	4.80	7.20	26.50	12.40	32.40	8.80	0.2717	0.3827	0.1964

[a]Volume standard temperature pressure. [b]CH_4 was not tested for. [c]LO-30SH cell. [d]Helium not used.
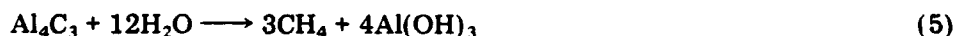
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hydrogen, and methane. Infrared spectroscopy, mass spectroscopy, and gas chromatography techniques were used. Using GC, the ratios of the amounts of hydrogen divided by the acetylene varied from 0.1 to 4.7 with an average ratio of 0.6. The ratio of methane to total acetylene and hydrogen varied from 0.04 to 0.4 with an average value of 0.15.

Discussion

Since acetylene can be generated from lithium carbide, and methane from aluminum carbide [2], the following reactions are suggested as having occurred inside the lithium–sulfur dioxide battery during incineration:

$$2Li + 2C \longrightarrow Li_2C_2 \tag{1}$$

$$4Al + 3C \longrightarrow Al_4C_3 \tag{2}$$

and when soaked with water:

$$Li_2C_2 + 2H_2O \longrightarrow C_2H_2 + 2LiOH \tag{3}$$

$$2Li + 2H_2O \longrightarrow H_2 + 2LiOH \tag{4}$$

$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3 \tag{5}$$

Since two moles of lithium are required to produce one mole of either acetylene or hydrogen, six dm^3 of hydrogen and acetylene gas at STP would be equivalent to 3.7 g of lithium, very close to the 3.5 g indicated as being present in the anode of an L0-26SH cell by Duracell [3].

Conclusions

In conclusion, almost all of the lithium of the anode can remain inside an incinerated cell, primarily in the form of both lithium and lithium carbide formed through the reaction of metallic lithium with the carbon of the current collector. More gas from water reactive chemicals is released than can be accounted for by just the lithium used as the anode. Since methane is also found in appreciable amounts, it is suggestive that this gas comes from a water-reactive aluminum compound such as aluminum carbide. The water reactive materials inside an incinerated battery cell are stable for months with a small decrease in reactivity with increased time. This decreased reactivity is no doubt due to the reaction of the cell contents with moisture from the air; cells showing no water-reactive materials were found to be much heavier than the others. Incinerated L0-26SH cells that did not release gas upon the addition of water usually weighed around 60 g as opposed to the usual 46 - 48 grams.

We feel that these results are of importance to anyone considering using incineration as a means of disposal of lithium–sulfur dioxide batteries, because the slow introduction of water into incinerated cells would, in turn,

release large quantities of flammable and explosive gases. Another area where these findings would be of value is in the extinguishment of fires where lithium–sulfur dioxide batteries are present. If most of the initial lithium metal can be accounted for within the cell, then the amount that escapes the cell in a fire should be minimal. We have applied Halon 1211, AFFF, water, and carbon dioxide to fires containing Duracell L0-26SH and L0-30SH lithium–sulfur dioxide cells and did not observe anything that could be attributed to a reaction of the fire extinguishment agent with the lithium of the cells.

Acknowledgements

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1 *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland, OH, 52 edn., 1971, p. D180.
2 T. Moeller, *Inorganic Chemistry*, Wiley, New York, 1952, p. 697.
3 *Duracell Lithium Battery Product Bull. No. 479*, 1982.

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